

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: A61K 7/06, 7/48	A1	(11) International Publication Number: WO 96/32918 (43) International Publication Date: 24 October 1996 (24.10.96)
(21) International Application Number: PCT/US96/04183 (22) International Filing Date: 27 March 1996 (27.03.96) (30) Priority Data: 08/426,332 21 April 1995 (21.04.95) US (71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors: TORGERSON, Peter, Marte; 4127 U.S. Route 35 N.W., Washington Courthouse, OH 43160 (US). DANZIGER, James, Lee; 9556 Parrot Place, Mason, OH 45040 (US). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: AU, BR, CA, CN, JP, KR, MX, TR, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: TOPICAL PERSONAL CARE COMPOSITION CONTAINING ALKENYL OR STYRENE END-CAPPED SILICONE GRAFTED COPOLYMER (57) Abstract <p>Topical personal care compositions containing aqueous or hydroalcoholic carriers and silicone grafted copolymers with acid-containing monomers characterized by substantially improved or eliminated hydrolysis of the silicone portion of the copolymer are obtained by the selection of specific types of silicone macromers for incorporation into the silicone grafted copolymer. The silicone macromers are selected from the group consisting of alkenyl end-capped silicone macromers and styrene end-capped silicone macromers, and combinations thereof. The silicone macromers are ethylenically unsaturated, polymerizable monomers having a styrene or alkenyl end-capped silicone group covalently bound to the ethylenically unsaturated portion of the monomer via the styrene or alkenyl end-cap.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LJ	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

TOPICAL PERSONAL CARE COMPOSITION CONTAINING ALKENYL OR STYRENE END-CAPPED SILICONE GRAFTED COPOLYMER

5

TECHNICAL FIELD

This invention relates to topical personal care compositions containing silicone grafted copolymers and an aqueous or hydroalcoholic carrier suitable for application to the skin or hair, wherein the silicone grafted copolymer is soluble or dispersible in the continuous phase of the carrier.

BACKGROUND OF THE INVENTION

The use of silicone grafted copolymers in a wide variety of topical care compositions, e.g. hair and skin care compositions, has become widely known. These polymers are useful for their film forming and adhesive properties, they can be used as adhesive agents in hair sprays, mousses, and lotions, as well as for a wide variety of skin care products such as cosmetics and skin conditioning compositions, wherein their film forming properties are used to smooth the skin or as an aid to deliver other ingredients to the skin. One of the primary benefits of silicone grafted copolymers is that the silicone portions provide improved tactile properties relative to conventional polymers. For example, hair treated with them retains its styled shape in accordance with the wishes of the user, yet feels softer than hair styled with conventional hair styling polymers. Skin treated with silicone grafted polymers feels smoother to the touch than skin treated with conventional polymers.

One of the most desirable and least costly ways to use silicone grafted copolymers is to formulate them into aqueous or hydroalcoholic carriers, wherein the silicone grafted copolymers is soluble in or otherwise stably distributed throughout the aqueous/hydroalcoholic phase. An alternate and also desirable type of composition provides the silicone grafted copolymer solubilized in a nonaqueous solvent, such as cyclomethicone or a hydrocarbon, which is emulsified in the form of droplets distributed throughout the aqueous or hydroalcoholic carrier. Whereas this type of formulation is useful and desirable for many types of products, it is more desirable and less expensive for many other products to use silicone grafted copolymers that are solubilized or stably dispersed in non-emulsified, non-droplet form in the aqueous or hydroalcoholic carrier.

One of the preferred types of silicone grafted copolymers for use in aqueous topical personal care compositions, especially hair spray compositions, contains

acrylic acid monomers and methacryloxy propyl end-capped silicone macromers. It is highly desirable to use acrylic acid monomers because the acid group provides a high degree of polarity which allows the polymer to be soluble or dispersible in water or hydroalcoholic carriers. Other highly polar monomers, such as many cationic monomers, can provide similar solubility to the polymer but tend to be more hygroscopic. This can result in the product becoming sticky during use, particularly during humid conditions. Unfortunately, it has been found that these silicone grafted copolymers tend to hydrolyze in the aqueous or hydroalcoholic products at an undesirably high rate, resulting in separation of the silicone portion from the remainder of the copolymer. Similar copolymers containing the same type of silicone macromer but not containing the acrylic acid monomer do not hydrolyze at such high rates. Therefore, it appears that the hydrolysis problem surprisingly only occurs when the polymer contains an acrylic acid or other acid-containing monomer.

Hydrolysis is of concern since a wide variety of products contain water as the primary or cosolvent for hair styling polymers and other hair and skin care adhesive polymers. It is a particularly concerning issue in view of the current trend toward developing products having high water content and reduced levels of volatile organic compounds (VOC's). Of particular interest is the trend toward regulation of product to contain reduced levels of VOC's, such as the 55% and 80% VOC regulations anticipated or already present in numerous countries. As the trend toward topical personal care products with reduced levels of VOC's continues, VOC-based formulas will be replaced in whole or in part with aqueous and hydroalcoholic formulas.

It is an object of this invention to provide aqueous and hydroalcoholic topical personal care compositions containing silicone grafted copolymers which have improved stability against hydrolysis. It is also an object of this invention to provide compositions as described above which contain acrylic acid or other acid-containing monomers in the silicone grafted copolymer, or which otherwise can provide the product attributes found in such copolymers. It is another object of this invention to provide compositions which meet the above objects and which contain relatively low or zero levels of volatile organic compounds. These and other benefits of the present invention as may be or become apparent to those in the art can be obtained by the invention described below.

Unless otherwise indicated, all percentages are calculated by weight of the total composition and all ratios are calculated on a weight basis. Unless otherwise indicated, ingredient amounts are based on the active level and therefore do not include carriers or by-products that may be included in commercial or otherwise available materials. The present invention may comprise, consist of, or consist

essentially of any of the essential and various optional and/or preferred ingredients and elements described herein. The terms "soluble" and "insoluble" shall refer to the solubility characteristics of a particular ingredient in the composition, unless otherwise specifically indicated. All viscosities and solubilities are determined at 5 25°C, unless otherwise specifically indicated. Also, unless otherwise indicated, all weight percentages of the compositions hereof are based on the total weight of the composition exclusive of any propellant that may be possibly incorporated into the product or otherwise contemplated.

SUMMARY OF THE INVENTION

10 Topical personal care compositions containing aqueous or hydroalcoholic carriers and silicone grafted copolymers characterized by substantially improved or eliminated hydrolysis of the silicone portion of the copolymer can be obtained in accordance with the present invention. It has been found that such compositions can be obtained by combining acid-containing monomers with the selection of specific 15 types of silicone macromers for incorporation into the silicone grafted copolymer. The silicone macromers hereof are selected from the group consisting of alkenyl end-capped silicone macromers and styrene end-capped silicone macromers, and combinations thereof. The silicone macromers are ethylenically unsaturated, polymerizable monomers having a styrene or alkenyl end-capped silicone group 20 covalently bound to the ethylenically unsaturated portion of the monomer via the styrene or alkenyl end-cap.

The compositions hereof can be used in a wide variety of topical personal care applications, including hair care, skin care, cosmetics, and personal cleansing compositions. They are especially useful for hair styling products, such as hair 25 sprays, hair lotions, hair tonics, mousses, hair rinses, and shampoos. Other useful, specific product applications include skin care compositions such as skin moisturizers and other skin conditioning compositions, sunscreens, sunless tanning compositions, skin cleansing compositions, anti-acne compositions, topical analgesic compositions, and other drug-containing topical skin compositions. Skin care compositions also 30 include cosmetics.

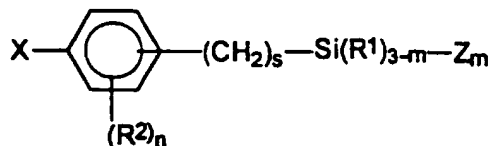
More specifically, the present invention provides topical personal care compositions containing silicone grafted copolymer having improved resistance against hydrolysis, wherein the compositions comprise:

- 35 (a) from about 0.1% to about 50%, by weight of the composition, of silicone grafted copolymer containing:
- (i) from about 1% to about 99%, by weight of the copolymer, of acid-containing monomers, said acids of the acid-containing monomers

preferably being selected from the group consisting of carboxylic acid and sulfonic acid, and combinations thereof;

(ii) from about 1% to about 50% of silicone macromers having the formula:

5

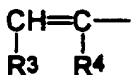


or



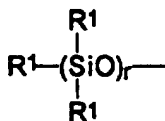
10

wherein: s is an integer from 0 to about 6; m is an integer from 1 to 3, R² is C1-C10 alkyl or C7-C10 alkylaryl; n is an integer from 0 to 4; X is an ethylenically unsaturated group of the formula :



15

wherein R³ is -H or C1-C6 alkyl; R⁴ is H or C1-C6 alkyl; Z is



20

wherein each R¹ independently is an alkyl, aryl or alkylaryl having from 1 to 10 carbon atoms, and r is an integer from about 4 to about 700, and combinations thereof;

(iii) from 0% to about 98% of additional monomers, and combinations thereof; and

25

(b) from about 1% to about 99.9%, by weight of the composition, of an aqueous or hydroalcoholic solvent for said silicone grafted copolymer suitable for application to the hair or skin, wherein said copolymer is soluble or dispersible in said solvent.

The present invention is described in more detail below in the Detailed Description of the Invention.

DETAILED DESCRIPTION OF THE INVENTION

The topical personal care compositions of the present invention generally comprise: (a) from about 0.1% to about 50%, by weight, of the styrene or alkenyl end-capped silicone grafted copolymer hereof, preferably from about 0.2% to about 20%, more preferably from about 0.5% to about 15%, even more preferably from about 1% to about 10%, most preferably from about 2% to about 8%; and (b) from about 1% to about 99.9%, by weight, of an aqueous or hydroalcoholic solvent for the silicone grafted copolymer suitable for application to the hair or skin, preferably from about 50% to about 99.8%, more preferably from about 60% to about 99.5%, even more preferably from about 70% to about 99%, most preferably from about 80% to about 98%. The silicone grafted copolymer is soluble or dispersible in the aqueous or hydroalcoholic solvent.

The topical personal care compositions hereof are, by definition, suitable for topical application to the skin or hair. By "suitable for topical application to the skin or hair" what is meant that the compositions are safe for topical application to the skin or hair when used in their intended manner and effective for delivering the copolymers hereof to the skin or hair in such a manner that the copolymer can provide its intended benefit.

Aqueous or Hydroalcoholic Solvent

The aqueous or hydroalcoholic solvent for the copolymers of the present invention can be water or a combination of water and one or more monohydric C1-C6 alcohols, preferably C2-C3 alcohols, more preferably C2 alcohol (i.e., ethanol). The levels of total aqueous or hydroalcoholic solvent are described above. By hydroalcoholic, what is meant is any mixture of water and one or more of the alcohols containing at least about 0.5%, by weight of the solvent, of water.

For hair care products in general, such as hair sprays and mousses, however, the compositions hereof will generally comprise at least about 5% water, preferably at least about 10% water, more preferably at least about 20% water.

In another aspect of this invention, the compositions hereof are characterized by reduced levels of volatile organic compounds (VOC's), and will comprise from about 40% to about 99.9% water and from 0% to about 80% of the monohydric alcohols, preferably from 0% to about 55% of the monohydric alcohols. In a particularly preferred embodiment for aerosol or nonaerosol hairspray compositions, the compositions will comprise from about 40% to about 75% water and from about 20% to about 55% monohydric alcohol, or from about 40% to about 95% water and from 0% to about 55% monohydric alcohol. In reduced VOC compositions, the total level of VOC's will preferably be no greater than about 80%, by weight of the composition, inclusive of propellants, preferably no greater than about 55%.

For purposes hereof, VOC's are defined as any organic compounds (including silicones) which either have: a vapor pressure at 20°C of 0.1 mm Hg or higher; or contain 12 or less carbon atoms. Conversely, organic compounds having a vapor pressure of less than 0.1 mm Hg under the same conditions or which contain more than 12 carbon atoms are defined herein as being nonvolatile.

The styrene and alkenyl end-capped silicone grafted copolymers hereof are soluble or dispersible in the aqueous or hydroalcoholic solvent. This is in contrast to the situation wherein the copolymer is not soluble or dispersible in the solvent, thereby existing in a separate or discontinuous phase from the solvent.

Additional solvents, cosolvents, and solubilizing aids may be incorporated into the compositions hereof to assist with solubilization of the copolymer without departing from the spirit or intent of the invention. Examples of such ingredients include, but are not limited to, di- and tri- hydric alcohols, surfactants and emulsifiers.

Styrene/Alkenyl End-Capped Silicone Grafted Copolymer

The silicone grafted copolymer (hereinafter sometimes referred to as "the copolymer") constitutes an essential component of the present invention. The term "copolymer", as used herein, refers to polymers derived by polymerization of two or more different species of monomers. The copolymers hereof are made by the copolymerization of one or more types of acid-containing monomers, one or more species of certain styrene or alkenyl end-capped silicone macromers (or a mixture thereof), and optionally one or more other types of monomers. For convenience, the copolymers hereof may sometimes be referred to as being derived from said monomers and macromers, meaning that the copolymer is made by copolymerization of said monomers and macromers. The term "monomer", as used herein, means ethylenically unsaturated compounds capable of being polymerized to form copolymers, as defined herein. The term "macromer", as used herein, shall refer to a monomer characterized by having a polymeric substituent. The essential macromers of the present invention are silicone macromers, meaning that the macromers have silicone as a polymeric substituent. Also, the copolymers hereof may sometimes be said to comprise said monomers and macromers, meaning that the copolymer comprises units corresponding to the indicated pre-polymerization monomers and macromers.

Acid-Containing Monomers

The copolymers hereof comprise from about 1% to about 99%, by weight of the copolymer, of acid-containing monomers. In general, the copolymers will preferably comprise from about 5% to about 90%, more preferably from about 10%

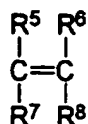
to about 80%, most preferably from about 15% to about 75%. The particular level of acid-containing monomer preferred for any specific composition can vary depending on the type of formulation and intended use, as well as the types and amounts of the other monomers and macromers in the copolymer and the molecular weight of the copolymer. For hair spray and other hair care compositions, for example, the copolymer preferably comprises from about 5% to about 50%, by weight of the copolymer, of acid-containing monomer, more preferably from about 10% to about 35%, most preferably from about 15% to about 25%.

The acid-containing monomers will preferably be selected from monomers containing acid groups selected from the group consisting of carboxylic acids and sulfonic acids, most preferably carboxylic acids. Other acid-containing monomers can also be used, including but not limited to phosphonic acid-containing monomers. Combinations of the above types of acid-containing monomers can also be used.

The acid-containing monomer units present in the final copolymer can be derived from polymerizable acid-containing starting monomers, or from polymerizable nonionic monomers which are modified subsequent to polymerization to the acid functionalities. Included within the term acid-containing monomers are the neutralized versions, i.e. salts, of the monomers hereof. Neutralization is discussed in more detail below.

Examples of acid-containing monomers include:

(i) Carboxylic acid-containing monomers, including those corresponding to the formula:



wherein: R^5 and R^6 independently are H or C1-C6 alkyl, preferably H or methyl; R^7 is H, C1-C6 alkyl, or a carboxylic moiety having up to about 12 carbon atoms, preferably H or methyl, or if R^7 is a carboxylic acid moiety, preferably acrylic acid; and R^8 is a carboxylic moiety having up to about 12 carbon atoms.

Specific examples of carboxylic acid-containing monomers include acrylic acid, methacrylic acid, maleic acid, maleic acid half ester, itaconic acid, fumaric acid, and crotonic acid, half esters of polybasic acid anhydride such as succinic anhydride, phthalic anhydride or the like reacted with a hydroxyl group-containing acrylate and/or methacrylate such as hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, and the like.

(ii) Sulfonic acid-containing monomers such as styrenesulfonic acid, and sulfoalkyl acrylates and methacrylates, preferably with C1-C6 alkyl groups, more preferably C2 alkyl groups, such as sulfoethyl acrylate, sulfoethyl methacrylate, and the like.

- 5 (iii) Phosphoric acid-containing monomers such as the phospho oxyalkyl acrylates and methacrylates, preferably with C1-C6 oxyalkyl groups, more preferably C1-C3 oxyalkyl. Specific examples include phospho-oxyethyl acrylate, phospho-oxyethyl methacrylate, 3-chloro-2-acid phospho-oxypropyl acrylate, phospho-oxypropyl methacrylate, and the like.

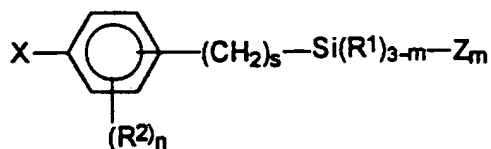
- 10 Preferred acid containing monomers are the carboxylic acids and the sulfonic acids. Most preferred are the carboxylic acids. Examples of highly preferred acid-containing monomers are acrylic acid, methacrylic acid, and styrenesulfonic acid. Especially preferred acid-containing monomers are acrylic acid and methacrylic acid.

Styrene and Alkenyl End-Capped Silicone Macromers

- 15 The copolymers hereof comprise from about 1% to about 50%, by weight of the copolymer, of styrene end-capped silicone macromers, alkenyl end-capped silicone macromers, or a combination thereof, preferably from about 2% to about 40%, more preferably from about 5% to about 40%, most preferably from about 5% to about 25%. By "styrene" or "alkenyl" end-capped silicone macromer what is
20 meant is that the macromer contains a silicone, i.e. polymeric siloxane or "polysiloxane" group, that is covalently bound to the monomer via a styrene group or an alkenyl group, respectively.

The preferred styrene end-capped silicone macromers and alkenyl end-capped macromers of the present invention have the formulas, respectively:

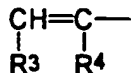
25



and

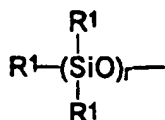


- 30 wherein: s is an integer from 0 to about 6, preferably 0, 1, or 2, more preferably 0 or 1; m is an integer from 1 to 3, preferably 1; R² is C1-C10 alkyl or C7-C10 alkylaryl, preferably C1-C6 alkyl or C7-C10 alkylaryl, more preferably C1-C2 alkyl; n is an integer from 0 to 4, preferably 0 or 1, more preferably 0; X is an ethylenically unsaturated group (prior to polymerization) of the formula:



wherein R^3 is H or C1-C6 alkyl, preferably H or C1-C2 alkyl, more preferably H; R^4 is H or C1-C6 alkyl, preferably H or C1-C2 alkyl, more preferably H or methyl; Z is:

5



wherein: each R^1 independently is an alkyl, aryl or alkylaryl having from 1 to 10 carbon atoms, preferably C1-C6 alkyl, more preferably C1-C2 alkyl, most preferably methyl; and r is an integer from about 4 to about 700, preferably from about 50 to about 500, more preferably from about 100 to about 300; and combinations thereof. For hair care compositions, such as hair sprays, r is most preferably from about 150 to about 200. The styrene end-capped silicone macromers are preferred.

The silicone portion of the macromer is preferably substituted at the para or meta positions of the aromatic ring relative to X, most preferably at the para position. If n is not 0, then the R^2 group or groups are preferably substituted at the meta positions. The ortho positions are preferably, but not necessarily, unsubstituted.

Styrene and alkenyl end-capped silicone macromers and methods for making them are well-known in the art. See, for example, Holohan, George, Barrie, and Parker, "Monofunctional Polydimethylsiloxane Oligomers For Graft Copolymerization", *Macromol. Chem. Phys.* 195, 2965-2979 (1994), which discloses silicone macromers wherein s = 0 for styrene end-capped macromers and wherein and s = 0 or an integer for alkenyl end-capped silicone macromers. Further disclosure relating to methods of making the silicone macromers hereof can be found in the Experimental section, below.

25 Additional Monomers

The copolymers hereof, in general, comprise from 0% to about 98%, by weight of the copolymer, of additional monomers other than the acid-containing monomers and styrene or alkenyl end-capped silicone macromers described above, preferably from 0% to about 80%, more preferably from 20% to about 70%. For hair care compositions, such as hair sprays, the copolymer preferably comprises from 40% to about 70% of additional monomers. The use of additional monomers can be especially desirable for increasing the Tg of the copolymer, as described in more detail below, or for adjusting the solubility of the copolymer, depending upon the

particular types and levels of the other copolymers and the type and amount of the aqueous or hydroalcoholic solvent. When used in whole or part for one or both of these purposes, the additional monomers will generally be used at a level of at least about 1%, by weight of the copolymer, more generally at least about 2%, preferably at least about 5%, more preferably at least about 10%.

A wide variety of the additional monomers can be used. These include nonionic monomers, cationic monomers, and amphoteric monomers. The nonionic monomers can be either low or high polarity monomers. The cationic monomers can be polymerized in the cationic state, or can be polymerized as a nonionic precursor which is then quaternized or otherwise made cationic subsequent to polymerization. If cationic monomers are to be used, it is preferred that the weight percentage of at least one of either the cationic or acid-containing monomers be no greater than about 10%, preferably no greater than about 5%, to minimize the occurrence of ionic interaction between the two charged groups.

Examples of low polarity nonionic monomers are: acrylic and methacrylic acid esters of C1-C24 alcohols, such as methanol, ethanol, allyl alcohol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol, cyclohexanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, oleyl alcohol, isobornyl alcohol, tetrahydrofurfuryl alcohol, and the like, the alcohols preferably having an average number of carbon atoms of from about 1-18, more preferably from about 1-12; styrene; alkylstyrenes, preferably with C1-C6 alkyls, such as t-butylstyrene; chlorostyrene; vinyl esters such as vinyl acetate and vinyl propionate; vinyl chloride; vinyl toluene; vinyl caprolactam; vinylidene chloride; acrylonitrile; alpha-alkylstyrenes, preferably with C1-C6 alkyl groups, such as alpha-methylstyrene; 1,3-dialkenes, such as butadiene and cyclohexadiene; ethylenically unsaturated hydrocarbons, preferably C1-C5 alkenes, such as ethylene and propylene; alkoxyalkyl (meth)acrylates, preferably with C1-C6 alkyl groups, such as methoxy ethyl (meth)acrylate, butoxyethyl (meth)acrylate; and alkyl vinyl ethers, preferably C1-C6 alkyl vinyl ethers, such as methyl vinyl ether. Other low polarity nonionic monomers include: acrylate and methacrylate derivatives such as di-acrylates and di-methacrylates, e.g. ethylene glycol di-acrylate, ethylene glycol di-methacrylate, 1,3-butyleneglycol di-acrylate and -methacrylate; and

diacetonacrylamide. As used herein, the clause "(meth)acrylate" shall mean that both "acrylate" and "methacrylate" are disclosed.

Preferred low polarity nonionic monomers include n-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, t-butylacrylate, t-butylmethacrylate, and mixtures thereof.

Exemplary high polarity nonionic monomers include; acrylamide; methacrylamide; N,N-dialkyl(meth)acrylamides, especially with C1-C6 alkyls, preferably methyl, such as N,N-dimethylacrylamide; N-alkyl acrylamides, especially with C1-C6 alkyls, such as N-t-butyl acrylamide and isopropylacrylamide; acrylate and methacrylate alcohols, especially C2-C6 (meth)acrylate alcohols, such as hydroxyethyl acrylate, hydroxyethylmethacrylate, hydroxypropylacrylate, and hydroxypropylmethacrylate; vinyl pyrrolidone, allyl alcohol, and vinyl alcohol (made by hydrolyzing vinyl acetate after polymerization).

Cationic monomers include quaternizable, amino-functional, ethylenically unsaturated monomers, such as the amino functional derivatives of styrene, acrylamide, methacrylamide, (meth)acrylates such as the C₁-C₅ alkyl esters of acrylic acid and methacrylic acid. Preferred are C₁-C₅ alkyl amines especially C₁-C₃ amines. It is preferred to use the tertiary amines. (e.g., trialkyl amines), though it is not meant to necessarily exclude monoalkyl amines, dialkyl amines, and other alkyl amine derivatives. Especially preferred are dimethyl amino C₁-C₃ alkyl amines. These monomers can be quaternized prior to or subsequent to polymerization, preferably subsequent to polymerization.

Cationic monomers include:

(i) monomers derived from acrylic acid or methacrylic acid, which is referred to hereinafter collectively as (meth)acrylic acid, and a quaternarized epihalohydrin product of a trialkylamine having 1 to 5 carbon atoms in the alkyl such as (meth)acryloxypropyltrimethylammonium chloride and (meth)acryloxypropyltriethylammonium bromide;

(ii) amine derivatives of (meth)acrylic acid or amine derivatives of (meth)acrylamide derived from (meth)acrylic acid or (meth)acrylamide and a dialkylalkanolamine having C1-C4 alkyl groups such as dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, or dimethylaminopropyl (meth)acrylamide; and

(iii) derivatives of the products of the group (ii) above by (1) neutralization with an acid such as hydrochloric acid, or lactic acid, (2) modification with a halogenated alkyl, such as methyl chloride, ethyl chloride, methyl bromide, or

ethyl iodide, (3) modification with a halogenated fatty acid ester such as ethyl monochloroacetate, or methyl monochloropropionate, and (4) modification with a dialkyl sulfate such as dimethyl sulfate, or diethyl sulfate.

Specific examples of such monomers include: (i) p-dimethylaminomethyl
5 styrene, p-dimethylaminoethyl styrene; (ii) dimethylaminomethyl acrylamide, dimethylaminopropyl acrylamide, dimethylaminopropyl methacrylamide, dimethylaminomethyl methacrylamide; dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, and dimethylaminopropyl (meth)acrylamide. Cationic monomers also include amine
10 derivatives of allyl compounds such as diallyldimethylammonium chloride and the like.

As discussed above, cationic monomers can be polymerized in cationic form, or as an alternative they can be polymerized in the form of their precursors, which are then modified to be cationic, for example, by a quaternizing agent (e.g.
15 ethyl monochloroacetate, dimethyl sulfate, etc.).

Examples of the amphoteric monomers include zwitterionized derivatives of the aforementioned amine derivatives of (meth)acrylic acids or the amine derivatives of (meth)acrylamide such as dimethylaminoethyl (meth)acrylate, dimethylaminopropyl(meth)acrylamide by a halogenated fatty acid salt such as
20 potassium monochloroacetate, sodium monobromopropionate, aminomethylpropanol salt of monochloroacetic acid, triethanolamine salts of monochloroacetic acid and the like; and amine derivatives of (meth)acrylic acid or (meth)acrylamide, as discussed above, modified with propanesultone.

These amphoteric monomers, like the aforementioned cationic monomers,
25 can be polymerized in amphoteric form or, as an alternative, they can also be polymerized in the form of their precursors, which are then converted into the amphoteric state.

Copolymers

The copolymers hereof should have a weight average molecular weight of at
30 least about 20,000, for purposes of providing effective adhesive or film forming properties upon application to the hair or skin. There is no upper limit for molecular weight except that which limits applicability of the invention for practical reasons, such as processing, aesthetic characteristics, formulateability, etc. In general, the weight average molecular weight will be less than about
35 10,000,000, more generally less than about 5,000,000, and preferably less than about 3,000,000. Preferably, the weight average molecular weight will be between about 50,000 and about 2,000,000, more preferably between about

75,000 and about 1,000,000, most preferably between about 100,000 and about 750,000. Molecular weight can be determined by gel permeation chromatography via universal calibration with refractive index and differential viscometric detection using polystyrene standards, or equivalent.

5 Preferably, the copolymer hereof when dried to form a film has a Tg of at least about -20°C, preferably at least about 20°C, so that they are not unduly sticky, or "tacky" to the touch. Preferably, the Tg is from about 20°C to about 120°C. As used herein, the abbreviation "Tg" refers to the glass transition
10 by techniques well known in the art, such as by differential scanning calorimetry (DSC) or dynamic mechanical analysis. Tg can be controlled by varying the level and type of the various acid-containing monomers and additional monomers that are used.

Methods for making silicone grafted copolymers have become well-known
15 in the published art. The present silicone grafted copolymers can be made in accordance with known processes, subject to the additional requirement that the starting monomers be chosen such that the final product will be constituted of acid-containing monomers and styrene end-capped silicone macromers as described above. Examples of processes for making silicone grafted polymers are
20 described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, and U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, both of which are incorporated herein by reference, and also in U.S. Patent 5,061,481, Suzuki et al., issued October 29, 1991, U.S. Patent 5,219,560, Suzuki et al., issued June 15, 1993, U.S. Patent 5,166,276, Hayama et al., issued November 24, 1992, U.S. Patent
25 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al., issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, EPO 0 412 707, Torgerson et al., granted February 4, 1994, EPO 0 412 704, Bolich et al., published February 13, 1991, EPO application 92918969.4, Peffly, filed August 18,
30 1992, EPO Application 92918839.9, Hozshuh, et al., filed August 18, 1992, and EPO Application 92919224.3, filed August 18, 1992, all of which are incorporated herein by reference.

In general, the copolymers of the present invention can be made by free
radical polymerization of silicone macromers with acid-containing monomers and
35 other monomers that may be used. The general principles of free radical polymerization methods are well understood. See, for example, Odian, "Principles of Polymerization", 2nd edition, John Wiley & Sons, 1981, pp. 179-

318. The desired monomers are all placed in a reactor, along with a sufficient amount of a mutual solvent so that when the reaction is complete the viscosity of the reaction is reasonable. Typical monomer loadings are from about 20% to about 50%. Undesired terminators, especially oxygen, are removed as needed.

5 This can be done by evacuation or by purging with an inert gas, such as argon or nitrogen. The initiator is introduced and the reaction brought to the temperature needed for initiation to occur, assuming thermal initiators are used. Alternatively, redox or radiation initiation can be used as desired. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved,

10 typically from a few hours to a few days. The solvent is then removed, usually by evaporation or by precipitating the copolymer by addition of a nonsolvent. The polymer is further purified, as needed.

The copolymers hereof will preferably be utilized in at least partially neutralized form. Neutralization can promote solubility or dispersibility of the polymer in the composition. In addition, use of the neutralized form aids in

15 removability of the copolymer from the hair or skin upon cleansing with shampoo, soap, detergent, or other cleansing product. In general, it is preferred that from about 10% to 100%, more preferably from about 20% to about 90%, even more preferably from about 40% to about 85%, of the acidic functionality of the

20 polymer be neutralized.

Any conventionally used base, organic or metallic, may be used for neutralization. Hydroxides of alkali metal and alkaline earth metal are suitable neutralizers for use with the silicone grafted copolymers. Preferred neutralizing agents for use in hair spray compositions of the present invention are potassium

25 hydroxide and sodium hydroxide. Examples of other suitable neutralizing agents which may be used include amines, especially amino alcohols such as 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), mono-isopropanolamine (MIPA), diisopropanol-amine (DIPA), triisopropanolamine (TIPA) and dimethyl

30 steramine (DMS). Mixtures of amines and bases (metallic or organic) may also be used.

Removal of unreacted silicone macromer, if any is present at undesirably high levels which can interfere with product performance, can be done by any

35 means known in the art. One method that can be used is supercritical fluid extraction, such as with supercritical carbon dioxide. Another generally

applicable method is membrane separation, performed in accordance with standard techniques of the art.

A purification method which can be particularly useful for the copolymers hereof is solvent extraction with a nonpolar solvent. Suitable solvents include C3-
5 C8 hydrocarbons, preferably C5-C6 hydrocarbons, such as hexane. Before performing the extraction, the polymer reaction product is precipitated out of the reaction solvent (e.g., with water), and dried. The extraction solvent is preferably heated to near or slightly above the average Tg of the non-silicone backbone portion of the polysiloxane-grafted polymer of the adhesive agent. The
10 temperature should be high enough so that the polymer softens, but not so high such that it congeals. The extraction solvent and reaction product can be mixed before, or after heating the solvent. The extraction solvent and polymer reaction product should be held with mixing and preferably in an excess of solvent, for a reasonable period to effectuate removal of the soluble materials. This period will
15 depend upon the reflux temperature of the solvent, the Tg of the copolymer, the temperature to which the solvent is actually heated, the desired level of removal of unreacted monomer and low viscosity material remaining after polymerization, and the number of cycles of solvent extraction to be performed. Typically, the solvent extraction periods will be from about one-half hour to about two hours,
20 more typically from about one-half hour to about one hour. The solvent can be removed after each cycle by conventional means, e.g., decanting, filtering, etc., with drying or distillation to remove trace extraction solvent remaining in the product after the final extraction cycle.

Analysis of the polymer reaction product and the extracted materials, and
25 the purified film-forming agent can be done by conventional analysis techniques known in the art. These include, for example, nuclear magnetic resource (NMR), infrared molecular spectroscopies, gel permeation/size exclusion chromatography, liquid chromatography, gas chromatography, atomic absorption and emission spectroscopies, and wet methods such as titration.

30 Topical Personal Care Compositions

A wide variety of topical personal care compositions are contemplated under the present invention, including both hair care compositions and skin care compositions. Hair care compositions include hair sprays (aerosol and nonaerosol), hair tonics, hair lotions, shampoos, hair rinses, and mousses. Skin
35 care compositions include skin moisturizers and other skin conditioning compositions, sunscreens, sunless tanning compositions, skin cleansing compositions, anti-acne compositions, topical analgesic compositions and other

drug-containing topical skin applications, and the like. Skin care compositions also include cosmetics and fragrances, especially those intended for use in the facial area. Cosmetics include, for example: foundations; eye make-up, such as mascara; and lip make-up. Fragrances include perfumes, colognes, and after-shaves.

5 Topical personal care compositions of the present invention include products wherein the copolymer is used as an adhesive to style hair, to modify the surface of the skin for skin conditioning purposes or for cosmetic appearance purposes. The copolymer hereof can also be used to facilitate delivery of an active ingredient
10 to the hair or skin. Substantivity to the skin or hair can be enhanced for such ingredients as a result of entrapment by the adhesive films the copolymers of the present invention can form upon curing. Examples of such active ingredients include drugs, cosmetic actives (e.g., hair or skin conditioners, dyes and pigments for cosmetics, perfumes and fragrances, and the like), sunscreen actives (including
15 physical sun-blocking actives such as zinc or titanium dioxide, as well as chemical sunscreens which protect the skin or hair by selective absorption of UV-A and/or UV-B rays), and sunless tanning agents.

 The compositions hereof can be formulated to include any of the ingredients typically known for use in the type of product that is desired, as well as any other
20 ingredients that may provide desirable benefits without interfering unduly with the function of the styrene end-capped silicone grafted copolymer hereof. A nonexclusive description of a variety of such ingredients for use in topical personal care compositions is provided below.

 The topical personal care compositions can contain a wide variety of volatile
25 materials including, but not limited to acetone, hydrocarbons (such as isobutane, hexane, decene), halogenated hydrocarbons (such as Freons), linalool, esters (such as ethyl acetate, dibutyl phthalate), and volatile silicon derivatives (especially siloxanes such as phenyl pentamethyl disiloxane, methoxypropyl heptamethyl cyclo-
30 tetrasiloxane, chloropropyl pentamethyl disiloxane, hydroxypropyl pentamethyl di-siloxane, cyclomethicones such as octamethyl cyclotetrasiloxane and decamethyl cyclopentasiloxane, and polydimethyl siloxanes, such as dimethicone having, for example, a viscosity at 25°C of about 15 centipoise or less), and mixtures thereof. Volatile materials such as these are commonly used in topical compositions, such as
 sprays, tonics, gels, and mousses.

35 Aerosol topical personal care compositions, such as mousses and aerosol hair sprays, can utilize any of the conventional propellants to deliver the material. Examples of suitable propellants include materials such as trichlorofluoromethane,

dichlorodifluoromethane, difluoroethane, dimethylether, propane, n-butane or isobutane. Aerosol as well as nonaerosol spray products may include a surfactant to enhance spray quality. Examples of suitable surfactants include nonionic, cationic, anionic surfactants, or mixtures thereof. Fluorosurfactants are also encompassed herein. Surfactants are particularly desirable for the spray product of the present invention, especially spray products such as hair spray, wherein the spray quality can affect product performance, since the compositions hereof have relatively low levels of volatile organic compounds and relatively high levels of water. The high water levels of the present compositions can otherwise adversely affect spray quality. If such a surfactant is used, it is preferably present at a level of from about 0.01% to about 7.5% by weight of the total composition. The level of propellant can be adjusted as desired. It is generally from about 3% to about 30% by total weight of the composition (weight basis inclusive of propellant) of mousse compositions and from about 15% to about 50% of the aerosol hair spray compositions. The propellant level in other product forms may vary widely, but is generally between about 3% and about 70%, by weight of the total composition.

Suitable spray containers are well known in the art and include conventional, non-aerosol pump sprays i.e., "atomizers," aerosol containers or cans having propellant, as described above, and also pump aerosol containers utilizing compressed air as the propellant. Pump aerosol containers are disclosed, for example, in U.S. Patents 4,077,441, March 7, 1978, Olofsson and 4,850,577, July 25, 1989, TerStegge, both incorporated by reference herein, and also in U.S. Serial No. 07/839,648, Gosselin, Lund, Sojka, and Lefebvre, filed February 21, 1992, "Consumer Product Package Incorporating A Spray Device Utilizing Large Diameter Bubbles. Pump aerosols hair sprays using compressed air are also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASSOON AIRSPRAY[®] hair sprays.

The compositions of the present invention can be in a wide variety of forms. For example, single phase compositions as well as emulsions wherein the silicone grafted copolymer is present in the aqueous or hydroalcoholic phase of the emulsion. Exemplary emulsions include, but are not limited to, oil-in-water, water-in-oil, water-in-oil-in-water, and oil-in-water-in-silicone emulsions. The silicone grafted copolymer hereof will be present in an aqueous or hydroalcoholic phase of the composition.

The compositions can cover a broad range of viscosities, preferably from about 1 cS to about 200,000 cS, at 25 °C.

Additional Components

A wide variety of additional components can be employed in the topical personal care compositions herein. Non-limiting examples include the following.

Pharmaceutical Actives

5 The compositions of the present invention can comprise a safe and effective amount of a pharmaceutical active. The phrase "safe and effective amount", as used herein, means an amount of an active high enough to significantly or positively modify the condition to be treated, but low enough to avoid serious side effects (at a reasonable benefit/risk ratio), within the scope of sound medical judgement. A safe and effective amount of the pharmaceutical active will vary with the specific active,
10 the ability of the composition to penetrate the active through the skin, the amount of composition to be applied, the particular condition being treated, the age and physical condition of the patient being treated, the severity of the condition, the duration of the treatment, the nature of concurrent therapy, and like factors.

15 The pharmaceutical actives which can be used in the compositions of the present invention preferably comprise from about 0.1% to about 20% by weight of the compositions, more preferably from about 0.1% to about 10%, and most preferably from about 0.1% to about 5%. Mixtures of pharmaceutical actives may also be used.

Nonlimiting examples of pharmaceutical actives can include the following:

20 Useful pharmaceutical actives in the compositions of the present invention include anti-acne drugs. Anti-acne drugs preferred for use in the present invention include the keratolytics such as salicylic acid, sulfur, lactic acid, glycolic, pyruvic acid, urea, resorcinol, and N-acetylcysteine; retinoids such as retinoic acid and its derivatives (e.g., cis and trans); antibiotics and antimicrobials such as benzoyl
25 peroxide, octopirox, erythromycin, zinc, tetracyclin, triclosan, azelaic acid and its derivatives, phenoxy ethanol and phenoxy propanol, ethylacetate, clindamycin and meclocycline; sebastats such as flavinoids; alpha and beta hydroxy acids; and bile salts such as scymnol sulfate and its derivatives, deoxycholate, and cholate. Preferred for use herein is salicylic acid.

30 Useful pharmaceutical actives in the compositions of the present invention include non-steroidal anti-inflammatory drugs (NSAIDS). The NSAIDS can be selected from the following categories: propionic acid derivatives; acetic acid derivatives; fenamic acid derivatives; biphenylcarboxylic acid derivatives; and oxicams. All of these NSAIDS are fully described in the U.S. Patent 4,985,459 to
35 Sunshine et al., issued January 15, 1991, incorporated by reference herein. Most preferred are the propionic NSAIDS including but not limited to aspirin, acetaminophen, ibuprofen, naproxen, benoxaprofen, flurbiprofen, fenoprofen,

fenbufen, ketoprofen, indoprofen, pirprofen, carprofen, oxaprozin, pranoprofen, miroprofen, tioxaprofen, suprofen, alminoprofen, tiaprofenic acid, fluprofen and bucloxic acid. Also useful are the steroidal anti-inflammatory drugs including hydrocortisone and the like.

- 5 Useful pharmaceutical actives in the compositions of the present invention include antipruritic drugs. Antipruritic drugs preferred for inclusion in compositions of the present invention include pharmaceutically-acceptable salts of methdilazine and trimeprazine. Useful pharmaceutical actives in the compositions of the present invention include anesthetic drugs. Anesthetic drugs preferred for inclusion
- 10 in compositions of the present invention include pharmaceutically-acceptable salts of lidocaine, bupivacaine, chlorprocaine, dibucaine, etidocaine, mepivacaine, tetracaine, dyclonine, hexylcaine, procaine, cocaine, ketamine, pramoxine and phenol. Useful pharmaceutical actives in the compositions of the present invention include antimicrobial drugs (antibacterial, antifungal, antiprotozoal and antiviral drugs).
- 15 Antimicrobial drugs preferred for inclusion in compositions of the present invention include pharmaceutically-acceptable salts of b-lactam drugs, quinolone drugs, ciprofloxacin, norfloxacin, tetracycline, erythromycin, amikacin, triclosan, doxycycline, capreomycin, chlorhexidine, chlortetracycline, oxytetracycline, clindamycin, ethambutol, metronidazole, pentamidine, gentamicin, kanamycin,
- 20 lineomycin, methacycline, methenamine, minocycline, neomycin, netilmicin, paromomycin, streptomycin, tobramycin, miconazole and amantadine. Antimicrobial drugs preferred for inclusion in compositions of the present invention include tetracycline hydrochloride, erythromycin estolate, erythromycin stearate (salt), amikacin sulfate, doxycycline hydrochloride, capreomycin sulfate, chlorhexidine
- 25 gluconate, chlorhexidine hydrochloride, chlortetracycline hydrochloride, oxytetracycline hydrochloride, clindamycin hydrochloride, ethambutol hydrochloride, metronidazole hydrochloride, pentamidine hydrochloride, gentamicin sulfate, kanamycin sulfate, lineomycin hydrochloride, methacycline hydrochloride, methenamine hippurate, methenamine mandelate, minocycline hydrochloride,
- 30 neomycin sulfate, netilmicin sulfate, paromomycin sulfate, streptomycin sulfate, tobramycin sulfate, miconazole hydrochloride, amantadine hydrochloride, amantadine sulfate, triclosan, octopirox, parachlorometa xyleneol, nystatin, tolnaftate and clotrimazole.

- 35 A wide variety of alpha-hydroxy acids and beta-hydroxy acids can be useful for pharmaceutical and cosmetic purposes for the skin, including for anti-aging, reduced dryness, skin exfoliation, and reduction in the appearance of wrinkles and fine lines. These include salicylic acid, glycolic acid, and lactic acid.

Also useful herein are sunscreen agents. A wide variety of suncreening agents are described in U.S. Patent No. 5,087,445, to Haffey et al., issued February 11, 1992; U.S. Patent No. 5,073,372, to Turner et al., issued December 17, 1991; U.S. Patent No. 5,073,371, to Turner et al. issued December 17, 1991; and Segarin, et al., at Chapter VIII, pages 189 et seq., of Cosmetics Science and Technology, all of which are incorporated herein by reference in their entirety. Included among those sunscreens are those selected from the group consisting of 2-ethylhexyl p-methoxycinnamate, 2-ethylhexyl N,N-dimethyl-p-aminobenzoate, p-aminobenzoic acid, 2-phenylbenzimidazole-5-sulfonic acid, octocrylene, oxybenzone, homomenthyl salicylate, octyl salicylate, 4,4'-methoxy-t-butylidibenzoylmethane, 4-isopropyl dibenzoylmethane, 3-benzylidene camphor, 3-(4-methylbenzylidene) camphor, titanium dioxide, zinc oxide, silica, iron oxide, and mixtures thereof.

Generally, the sunscreens can comprise from about 0.5% to about 20% of the compositions useful herein. Exact amounts will vary depending upon the sunscreen chosen and the desired Sun Protection Factor (SPF). SPF is a commonly used measure of photoprotection of a sunscreen against erythema. See Federal Register, Vol. 43, No. 166, pp. 38206-38269, August 25, 1978, which is incorporated herein by reference in its entirety.

Also useful in the present invention are sunless tanning agents including dihydroxyacetone, glyceraldehyde, indoles and their derivatives, and the like. These sunless tanning agents may also be used in combination with the sunscreen agents.

Other useful actives include skin bleaching (or lightening) agents including but not limited to hydroquinone, ascorbic acid, kojic acid and sodium metabisulfite.

Other useful actives which are especially useful for hair care compositions include anti-dandruff actives such as zinc pyrithione, octopirox, selenium disulfide, sulfur, coal tar, and the like.

Zinc pyrithione and triclosan, as well as other anti-bacterials, may also be used in anti-perspirant compositions and deodorant compositions for use on the body, especially in the underarm area.

30 Conditioners

The compositions of the present invention can comprise a wide variety of conditioning agents for the hair or skin. The conditioning agents are typically used at a level of from about 0.05% to about 20%, by weight of the composition, preferably from about 0.1% to about 10%, more preferably from about 0.5% to about 5%.

35 Nonvolatile, as used herein, has the meaning as defined above.

Conditioning agents useful herein, and especially useful for hair care and skin care compositions, include nonvolatile conditioning fluids, such as hydrocarbons, silicone fluids, fatty esters, and fatty alcohols, as well as cationic materials.

5 The conditioning fluids will generally have a viscosity of about 3 million cs or less, preferably about 2 million cs or less, more preferably about 1.5 million cs or less.

Conditioning fluids include liquids selected from the group consisting of hydrocarbon oils and fatty esters. The fatty esters include compounds characterized by having at least 10 carbon atoms, and include esters with hydrocarbyl chains
10 derived from fatty acids or alcohols, e.g., mono-esters, polyhydric alcohol esters, and di- and tri-carboxylic acid esters. The hydrocarbyl radicals of the fatty esters hereof can also include or have covalently bonded thereto other compatible functionalities, such as amides and alkoxy moieties (e.g., ethoxy or ether linkages, etc.).

Hydrocarbon oils include cyclic hydrocarbons, straight chain aliphatic
15 hydrocarbons (saturated or unsaturated), and branched chain aliphatic hydrocarbons (saturated or unsaturated). Straight chain hydrocarbon oils will preferably contain from about 12 to about 19 carbon atoms, although it is not necessarily meant to be limit the hydrocarbons to this range. Branched chain hydrocarbon oils can and typically may contain higher numbers of carbon atoms. Also encompassed herein are
20 polymeric hydrocarbons of alkenyl monomers, such as C_2-C_6 alkenyl monomers. Specific examples of suitable materials include paraffin oil, mineral oil, saturated and unsaturated dodecane, saturated and unsaturated tridecane, saturated and unsaturated tetradecane, saturated and unsaturated pentadecane, saturated and unsaturated hexadecane, and mixtures thereof. A preferred hydrocarbon polymer is polybutene,
25 such as the copolymer of isobutylene and butene. A commercially available material of this type is L-14 polybutene from Amoco Chemical Co. (Chicago, Illinois, U.S.A.).

Monocarboxylic acid esters hereof include esters of alcohols and/or acids of the formula $R'COOR$ wherein alkyl or alkenyl radicals and the sum of carbon atoms
30 in R' and R is at least 10, preferably at least 20.

Fatty esters include, for example, alkyl and alkenyl esters of fatty acids having aliphatic chains with from about 10 to about 22 carbon atoms, and alkyl and alkenyl fatty alcohol carboxylic acid esters having an alkyl and/or alkenyl alcohol-derived aliphatic chain with about 10 to about 22 carbon atoms, and combinations thereof.
35 Examples include isopropyl isostearate, hexyl laurate, isohexyl laurate, isohexyl palmitate, isopropyl palmitate, decyl oleate, isodecyl oleate, hexadecyl stearate, decyl stearate, isopropyl isostearate, dihexyldecyl adipate, lauryl lactate, myristyl lactate,

cetyl lactate, oleyl stearate, oleyl oleate, oleyl myristate, lauryl acetate, cetyl propionate, and oleyl adipate. The mono-carboxylic acid ester however need not necessarily contain at least one chain with at least 10 carbon atoms, so long as the total number of aliphatic chain carbon atoms is at least 10. Examples include

5 diisopropyl adipate, diisohexyl adipate, and diisopropyl sebacate.

Di- and tri-alkyl and alkenyl esters of carboxylic acids can also be used. These include, for example, esters of C₄-C₈ dicarboxylic acids such as C₁-C₂₂ esters (preferably C₁-C₆) of succinic acid, glutaric acid, adipic acid, hexanoic acid, heptanoic acid, and octanoic acid. Specific examples include isocetyl stearyl

10 stearate, diisopropyl adipate, and tristearyl citrate.

Polyhydric alcohol esters include alkylene glycol esters, for example ethylene glycol mono and di-fatty acid esters, diethylene glycol mono- and di-fatty acid esters, polyethylene glycol mono- and di-fatty acid esters, propylene glycol mono- and di-fatty acid esters, polypropylene glycol monooleate, polypropylene glycol 2000

15 monostearate, ethoxylated propylene glycol monostearate, glyceryl mono- and di-fatty acid esters, polyglycerol poly-fatty acid esters, ethoxylated glyceryl monostearate, 1,3-butylene glycol monostearate, 1,3-butylene glycol distearate, polyoxyethylene polyol fatty acid ester, sorbitan fatty acid esters, and polyoxyethylene sorbitan fatty acid esters are satisfactory polyhydric alcohol esters for use

20 herein.

Glycerides include mono-, di-, and tri-glycerides. More specifically, included are the mono-, di-, and tri-esters of glycerol and long chain carboxylic acids, such as C₁₀-C₂₂ carboxylic acids. A variety of these types of materials can be obtained from vegetable and animal fats and oils, such as castor oil, safflower oil, cottonseed oil,

25 corn oil, olive oil, cod liver oil, almond oil, avocado oil, palm oil, sesame oil, lanolin and soybean oil. Synthetic oils include triolein and tristearin glyceryl dilaurate. Preferred glycerides are di-, and tri-glycerides. Especially preferred are triglycerides.

Other conditioning agents fluids include fatty alcohols, preferably C₁₀-C₂₂ alcohols, such as stearyl and cetyl alcohols.

30 Still other conditioning agents for hair and/or skin include urea; guanidine; aloe vera in any of its variety of forms (e.g., aloe vera gel); polyhydroxy alcohols such as sorbitol, glycerol, hexanetriol, propylene glycol, butylene glycol, hexylene glycol and the like; polyethylene glycols; sugars and starches; sugar and starch derivatives (e.g., alkoxylated glucose); hyaluronic acid; lactamide monoethanolamine; acetamide

35 monoethanolamine; and mixtures thereof.

Silicone Conditioning Agent

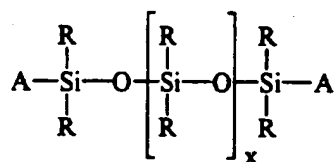
An optional component of the present invention is a nonvolatile, silicone conditioning agent.

The silicone conditioning agent for use herein will preferably have an average viscosity of from about 1,000 to about 2,000,000 centistokes at 25°C, more preferably from about 10,000 to about 1,800,000, even more preferably from about 100,000 to about 1,500,000. The viscosity of silicones herein can, in general, be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July 20, 1970.

The silicone conditioning agent will typically be used in the compositions hereof at levels of from about 0.05% to about 10% by weight of the composition, preferably from about 0.1% to about 10%, more preferably from about 0.5% to about 8%, most preferably from about 0.5% to about 5%.

Suitable insoluble, nonvolatile silicone conditioning agents include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and mixtures thereof. Other insoluble, nonvolatile silicones can also be used. The silicones hereof can be silicone fluids or silicone gums. The term "silicone fluid" shall mean flowable silicone materials having a viscosity of less than 1,000,000 centistokes at 25°C. Generally, the viscosity of the fluid will be between about 5 and 1,000,000 centistokes at 25°C, preferably between about 10 and about 100,000. Silicone gumds are described in more detail below.

Silicone fluids hereof include polyalkyl or polyaryl siloxanes with the following structure:



wherein R is alkyl or aryl, and x is an integer from about 1 to about 8,000, preferably from about 5 to about 8,000. "A" represents groups which block the ends of the silicone chains.

The alkyl or aryl groups substituted on the siloxane chain (R) or at the ends of the siloxane chains (A) may have any structure as long as the resulting silicones remain fluid at room temperature, are hydrophobic, are neither irritating, toxic nor otherwise harmful when applied to the hair, are compatible with the other components of the composition, are chemically stable under normal use and storage conditions, and are capable of being deposited on and of conditioning hair.

Suitable A groups include methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R groups on the silicone atom may represent the same group or different groups. Preferably, the two R groups represent the same group. Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred
5 silicones are polydimethyl siloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane is especially preferred.

The nonvolatile polyalkylsiloxane fluids that may be used include, for example, polydimethylsiloxanes. These siloxanes are available, for example, from the General Electric Company in their Viscasil^R and SF 96 series, and from Dow
10 Corning in their Dow Corning 200 series.

The polyalkylaryl siloxane fluids that may be used, also include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

15 The polyether siloxane copolymers that may be used include, for example, a polypropylene oxide modified polydimethylsiloxane (e.g., Dow Corning DC-1248) although ethylene oxide or mixtures of ethylene oxide and propylene oxide may also be used. The ethylene oxide and polypropylene oxide level must be sufficiently low to prevent solubility in water and the composition hereof.

20 Another silicone material that can be especially useful in the silicone conditioning agents is insoluble silicone gum. The term "silicone gum", as used herein, means polyorganosiloxane materials having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. Silicone gums are described by Petrarch and others including U.S. Patent 4,152,416, Spitzer et al., issued May 1, 1979 and Noll,
25 Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968. Also describing silicone gums are General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. All of these described references are incorporated herein by reference. The "silicone gums" will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and
30 about 1,000,000. Specific examples include polydimethylsiloxane, (polydimethylsiloxane) (methylvinylsiloxane) copolymer, poly(dimethylsiloxane) (diphenyl siloxane)(methylvinylsiloxane) copolymer and mixtures thereof.

Cationic Polymer Hair Conditioning Agent

35 The compositions of the present invention can also comprise cationic polymer conditioning agents. The polymeric cationic conditioning agents hereof will generally be used at levels of from about 0.05% to about 5%, preferably from about 0.1% to about 4%, more preferably from about 0.2% to about 3%, by weight, of the shampoo

composition. The cationic conditioning polymers are preferably water soluble. By "water soluble" cationic organic polymer, what is meant is a polymer which is sufficiently soluble in water to form a substantially clear solution to the naked eye at a concentration of 0.1% in water (distilled or equivalent) at 25°C. Preferably, the polymer will be sufficiently soluble to form a substantially clear solution at 0.5% concentration, more preferably at 1.0% concentration. The cationic polymers hereof will generally have a weight average molecular weight which is at least about 5,000, typically at least about 10,000, and up to about 10 million. Preferably, the molecular weight is from about 100,000 to about 2 million. The cationic polymers can generally be characterized by having have cationic nitrogen-containing moieties such as quaternary ammonium or cationic amino moieties, or a mixture thereof. Any anionic counterions can be utilized for the cationic polymers so long as the water solubility criteria is met. Suitable counterions include halides (e.g., Cl-, Br-, I-, or F-, preferably Cl-, Br-, or I-), sulfate, and methylsulfate. Others can also be used, as this list is not exclusive.

The cationic nitrogen-containing moiety will be present generally as a substituent, on a fraction of the total monomer units of the cationic hair conditioning polymers. Thus, the cationic polymer can comprise copolymers, terpolymers, etc. of quaternary ammonium or cationic amine-substituted monomer units and other non-cationic units referred to herein as spacer monomer units. Such polymers are known in the art, and a variety can be found in the CTFA Cosmetic Ingredient Dictionary, 3rd edition, edited by Estrin, Crosley, and Haynes, (The Cosmetic, Toiletry, and Fragrance Association, Inc., Washington, D.C., 1982).

Suitable cationic polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as acrylamide, methacrylamide, alkyl and dialkyl acrylamides, alkyl and dialkyl methacrylamides, alkyl acrylate, alkyl methacrylate, vinyl caprolactone, and vinyl pyrrolidone. The alkyl and dialkyl substituted monomers preferably have C₁-C₇ alkyl groups, more preferably C₁-C₃ alkyl groups. Other suitable spacer monomers include vinyl esters, vinyl alcohol (made by hydrolysis of polyvinyl acetate), maleic anhydride, propylene glycol, and ethylene glycol.

The cationic amines can be primary, secondary, or tertiary amines, depending upon the particular species and the pH of the shampoo. In general, secondary and tertiary amines, especially tertiary amines, are preferred.

Amine-substituted vinyl monomers can be polymerized in the amine form, and then optionally can be converted to ammonium by a quaternization reaction. Amines

can also be similarly quaternized subsequent to formation of the polymer. For example, tertiary amine functionalities can be quaternized by reaction with a salt of the formula R'X wherein R' is a short chain alkyl, preferably a C₁-C₇ alkyl, more preferably a C₁-C₃ alkyl, and X is an anion which forms a water soluble salt with the quaternized ammonium.

Suitable cationic amino and quaternary ammonium monomers include, for example, vinyl compounds substituted with dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, monoalkylaminoalkyl acrylate, monoalkylaminoalkyl methacrylate, trialkyl methacryloxyalkyl ammonium salt, trialkyl acryloxyalkyl ammonium salt, diallyl quaternary ammonium salts, and vinyl quaternary ammonium monomers having cyclic cationic nitrogen-containing rings such as pyridinium, imidazolium, and quaternized pyrrolidone, e.g., alkyl vinyl imidazolium, alkyl vinyl pyridinium, alkyl vinyl pyrrolidone salts. The alkyl portions of these monomers are preferably lower alkyls such as the C₁-C₃ alkyls, more preferably C₁ and C₂ alkyls.

Suitable amine-substituted vinyl monomers for use herein include dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, dialkylaminoalkyl acrylamide, and dialkylaminoalkyl methacrylamide, wherein the alkyl groups are preferably C₁-C₇ hydrocarbyls, more preferably C₁-C₃, alkyls.

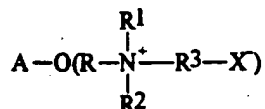
The cationic polymers hereof can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

Suitable cationic hair conditioning polymers include, for example: copolymers of 1-vinyl-2-pyrrolidone and 1-vinyl-3-methylimidazolium salt (e.g., chloride salt) (referred to in the industry by the Cosmetic, Toiletry, and Fragrance Association, "CTFA", as Polyquaternium-16), such as those commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under the LUVIQUAT tradename (e.g., LUVIQUAT FC 370); copolymers of 1-vinyl-2-pyrrolidone and dimethylaminoethyl methacrylate (referred to in the industry by CTFA as Polyquaternium-11) such as those commercially available from Gaf Corporation (Wayne, NJ, USA) under the GAFQUAT tradename (e.g., GAFQUAT 755N); cationic diallyl quaternary ammonium-containing polymers, including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively; and mineral acid salts of amino-alkyl esters of homo- and co-polymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, as described in U.S. Patent 4,009,256, incorporated herein by reference.

Other cationic polymers that can be used include polysaccharide polymers, such as cationic cellulose derivatives and cationic starch derivatives.

Cationic polysaccharide polymer materials suitable for use herein include those of the formula:

5



wherein: A is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual,

R is an alkylene oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or
10 combination thereof,

R¹, R², and R³ independently are alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms, and the total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in R¹, R² and R³) preferably being about 20 or less, and

15 X is an anionic counterion, as previously described.

Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR^R and LR^R series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10. Another type of cationic cellulose includes the poly-
20 meric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted opoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200.

Other cationic polymers that can be used include cationic guar gum
25 derivatives, such as guar hydroxypropyltrimonium chloride (commercially available from Celanese Corp. in their Jaguar^R series). Other materials include quaternary nitrogen-containing cellulose ethers (e.g., as described in U.S. Patent 3,962,418, incorporated by reference herein), and copolymers of etherified cellulose and starch (e.g., as described in U.S. Patent 3,958,581, incorporated by reference herein).

30 Cationic Surfactant Conditioning Agent

Cationic surfactants useful herein as conditioning agents include quaternary ammonium salts or the salts of fatty amines. Preferred quaternary ammonium salts are dialkyl dimethyl ammonium chlorides, wherein the alkyl groups have from 12 to 22 carbon atoms and are derived from long-chain fatty acids. Representative
35 examples of quaternary ammonium salts include ditallow dimethyl ammonium

chloride, ditallow dimethyl ammonium methyl sulfate, dihexadecyl dimethyl ammonium chloride, and di(hydrogenated tallow) ammonium chloride. Other quaternary ammonium salts useful herein are dicationics such as tallow propane diammonium dichloride. Quaternary imidazolinium salts are also useful herein.

- 5 Examples of such materials are those imidazolinium salts containing C12-22 alkyl groups such as 1-methyl-1-[(stearylamine)ethyl]-2-heptadecyl-4, 5-dihydroimidazolinium chloride, 1-methyl-1-[(palmitoylamine)ethyl]-2-octadecyl-4,5-dihydroimidazolinium chloride and 1-methyl-1-[(tallowamine)-ethyl]-2-tallow-imidazolinium methyl sulfate. Also useful herein are salts of fatty amines. Examples
10 of such compounds include stearylamine hydrochloride, soyamine hydrochloride, and stearylamine formate. Useful conditioning agents are disclosed in U.S. Patent No. 4,387,090, to Bolich, issued June 7, 1983, which is incorporated by reference herein.

Cationic surfactant conditioning agents are generally used at a level of from about 0.1% to about 5%, by weight of the composition.

15 Surfactants

- Surfactants are optional ingredients in the compositions of the invention. When present, the surfactant typically comprises from about 0.05% to about 50% of the composition. Surfactants are especially useful in cleansing compositions, such as shampoos and skin cleansing compositions, and can be used for a wide variety of
20 other purposes in these and other types of compositions hereof. Exemplary uses include emulsifiers, solubilizers of other ingredients, and conditioning (particularly cationic surfactants. For a shampoo or other cleansing composition, the surfactant level is preferably from about 5% to about 30%, more preferably from 12% to about 25%, of the composition. For conditioners, the preferred level of surfactant is from
25 about 0.05% to about 5%. Surfactants useful in compositions of the present invention include anionic, nonionic, cationic, and amphoteric surfactants. A wide variety of surfactants useful herein are disclosed in U.S. Patent No. 5,151,209, to Mc Call et al., issued September 29, 1992; U.S. Patent No. 5,151,210, to Steuri et al., issued September 29, 1992; and U.S. Patent No. 5,120,532, to Wells et al., issued
30 June 9, 1992, all of which are incorporated by reference herein.

- Anionic detergents useful herein include alkyl and alkyl ether sulfates. These materials typically have the respective formulae ROSO_3M and $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$, wherein R is alkyl or alkenyl of from about 10 to about 20 carbon atoms, x is 1 to 10, and M is a water-soluble cation such as ammonium, sodium, potassium and
35 triethanolamine.

Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula:

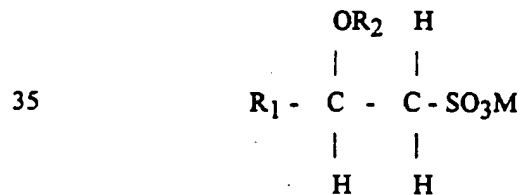


wherein R_1 is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 12 to about 18, carbon atoms; and M is a cation. Important examples are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, and n-paraffins, having about 8 to about 24 carbon atoms, preferably about 12 to about 18 carbon atoms and a sulfonating agent, e.g., SO_3 , H_2SO_4 , oleum, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated C_{12-18} n-paraffins.

Additional examples of anionic synthetic surfactants which come within the terms of the present invention are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other anionic synthetic surfactants of this variety are set forth in U.S. Patents 2,486,921; 2,486,922; and 2,396,278.

Still other anionic synthetic surfactants include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulfosuccinamate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinamate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl esters of sodium sulfosuccinic acid.

Other suitable anionic surfactants utilizable herein are olefin sulfonates having about 12 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of α -olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sultones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The α -olefins from which the olefin sulfonates are derived are mono-olefins having about 12 to about 24 carbon atoms, preferably about 14 to about 16 carbon atoms. Another class of anionic organic surfactants are the β -alkyloxy alkane sulfonates. These compounds have the following formula:



where R₁ is a straight chain alkyl group having from about 6 to about 20 carbon atoms, R₂ is a lower alkyl group having from about 1 (preferred) to about 3 carbon atoms, and M is a water-soluble cation as hereinbefore described.

Many additional nonsoap synthetic anionic surfactants are described in 5 McCutcheon's, Detergents and Emulsifiers, 1984 Annual, published by Allured Publishing Corporation, which is incorporated herein by reference. Also U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, discloses many other anionic as well as other surfactant types and is incorporated herein by reference. Soaps can also be utilized as anionic surfactants.

10 Nonionic surfactants, can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. Examples of classes of nonionic surfactants are:

1. Those derived from the condensation of ethylene oxide with the 15 product resulting from the reaction of propylene oxide and ethylene diamine products.

2. The condensation product of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from about 20 10 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 10 to about 14 carbon atoms.

3. Long chain tertiary amine oxides such as those corresponding to the following general formula:



25 wherein R₁ contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and R₂ and R₃ contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals (the arrow in the formula is a conventional 30 representation of a semipolar bond).

4. Long chain tertiary phosphine oxides corresponding to the following general formula:



35 wherein R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety and R' and R'' are each alkyl or

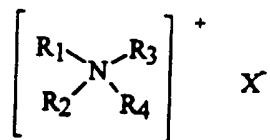
monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms. The arrow in the formula is a conventional representation of a semipolar bond.

5 5. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from about 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety. Examples include: octadecyl methyl sulfoxide, 2-ketotridecyl methyl sulfoxide, 3,6,9-triaoctadecyl 2-hydroxyethyl sulfoxide, dodecyl methyl sulfoxide, oleyl 3-hydroxypropyl sulfoxide, tetra decyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

15 6. N-Polyhydroxy fatty acid amides, such as the polyhydroxyhydrocarbyl C9-C19 fatty acid amides having polyhydroxy functionalities with at least three hydroxy groups, preferably derived from reducing sugars such as glucose, fructose, maltose, lactose, and the like. Surfactants of this type are disclosed in US Patent 2,965,576, E. R. Wilson, issued December 20, 1960, incorporated herein by reference.

20 Cationic surfactants useful in compositions of the present invention, particularly the conditioner compositions, contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention. Cationic surfactants among those useful herein are disclosed in the following documents, all incorporated by reference herein: M.C. Publishing Co., McCutcheon's Detergents & Emulsifiers, (North American edition 25 1979); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 3,929,678, Laughlin, et al., issued December 30, 1975; U.S. Patent 3,959,461, Bailey, et al., issued May 25, 1976; and U.S. Patent 4,387,090, Bolich, Jr., issued June 7, 1983. If included in the compositions of the 30 present invention, the cationic surfactant is generally present at from about 0.05% to about 5%.

 Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:



wherein R₁-R₄ are independently an aliphatic group of from about 1 to about 22 carbon atoms, or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having from about 12 to about 22 carbon atoms; and X is an anion selected from halogen, acetate, phosphate, nitrate and alkylsulfate radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those of about 12 carbons, or higher, can be saturated or unsaturated.

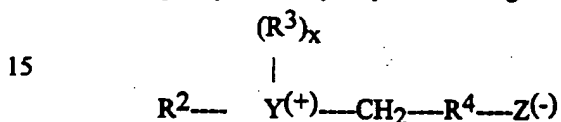
Other quaternary ammonium salts useful herein are diquaternary ammonium salts, such as tallow propane diammonium dichloride.

Quaternary ammonium salts include dialkyldimethyl-ammonium chlorides, wherein the alkyl groups have from about 12 to about 22 carbon atoms and are derived from long-chain fatty acids, such as hydrogenated tallow fatty acid (tallow fatty acids yield quaternary compounds wherein R₁ and R₂ have predominately from 16 to 18 carbon atoms). Examples of quaternary ammonium salts useful in the present invention include ditallowdimethyl ammonium chloride, ditallowdimethyl ammonium methyl sulfate, dihexadecyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium chloride, dioctadecyl dimethyl ammonium chloride, diecosyl dimethyl ammonium chloride, didocosyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium acetate, dihexadecyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium acetate, ditallow dipropyl ammonium phosphate, ditallow dimethyl ammonium nitrate, di(coconutalkyl) dimethyl ammonium chloride, and stearyl dimethyl benzyl ammonium chloride. Ditallow dimethyl ammonium chloride, dicetyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride and cetyl trimethyl ammonium chloride are preferred quaternary ammonium salts useful herein. Di-(saturated or unsaturated tallow) dimethyl ammonium chloride is a particularly preferred quaternary ammonium salt.

Salts of primary, secondary and tertiary fatty amines are also suitable cationic surfactant materials. The alkyl groups of such amines preferably have from about 12 to about 22 carbon atoms, and may be substituted or unsubstituted. Such amines, useful herein, include stearamido propyl dimethyl amine, diethyl amino ethyl stearamide, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated (5 moles

E.O.) stearylamine, dihydroxy ethyl stearylamine, and arachidylbehenylamine. Suitable amine salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts. Such salts include stearylamine hydrochloride, soyamine chloride, stearylamine formate, N-tallowpropane diamine dichloride and stearamidopropyl dimethylamine citrate. Cationic amine surfactants included among those useful in the present invention are disclosed in U.S. Patent 4,275,055, Nachtigal, et al., issued June 23, 1981, incorporated by reference herein.

Amphoteric surfactants, include those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



wherein R^2 contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R^3 is an alkyl or monohydroxyalkyl group containing about 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom; R^4 is an alkylene or hydroxyalkylene of from about 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Other amphoterics such as betaines are also useful in the present invention. Examples of betaines useful herein include the high alkyl betaines, such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alpha carboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl bis-(2-hydroxyethyl) carboxymethyl betaine, stearyl bis-(2-hydroxypropyl) carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, and lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine. The sulfobetaines may be represented by coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxyethyl) sulfopropyl betaine and the like; amidobetaines and amidosulfobetaines, wherein the $RCONH(CH_2)_3$ radical is attached to the nitrogen atom of the betaine are also useful in this invention.

Other examples of amphoteric surfactants which can be used in the compositions of the present invention are those which are broadly described as

derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate.

- 5 Examples of compounds falling within this definition are sodium 3-dodecylaminopropionate, sodium 3-dodecylamino propane sulfonate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold
10 under the trade name "Miranol" and described in U.S. Patent 2,528,378.

Thickening and Suspending Agents

The compositions of the present invention can comprise a wide variety of rheological modifiers as thickening an/or suspending agents. Exemplary ingredients of this type are described below.

- 15 The compositions may include gel vehicle materials. These are particularly useful for use in products such as hair rinses, creams and lotions.

Gel vehicles can comprise two essential components: a lipid vehicle material and a cationic surfactant vehicle material. Cationic surfactant materials are described in detail below. Gel vehicles are generally described in the following documents, all
20 incorporated by reference herein: Barry, "The Self Bodying Action of the Mixed Emulsifier Sodium Dodecyl Sulfate/Cetyl Alcohol", 28 J. of Colloid and Interface Science 82-91 (1968); Barry, et al., "The Self-Bodying Action of Alkyltrimethylammonium Bromides/Cetostearyl Alcohol Mixed Emulsifiers; Influence of Quaternary Chain Length", 35 J. of Colloid and Interface Science 689-
25 708 (1971); and Barry, et al., "Rheology of Systems Containing Cetomacrogol 1000 - Cetostearyl Alcohol, I. Self Bodying Action", 38 J. of Colloid and Interface Science 616-625 (1972).

The carrier may incorporate one or more lipid vehicle materials, regardless of whether it also contains a cationic surfactant, which are essentially water-insoluble,
30 and contain hydrophobic and hydrophilic moieties. Lipid vehicle materials include naturally or synthetically-derived acids, acid derivatives, alcohols, esters, ethers, ketones, and amides with carbon chains of from about 12 to about 22, preferably from about 16 to about 18, carbon atoms in length. Fatty alcohols and fatty esters are preferred; fatty alcohols are particularly preferred.

- 35 Preferred esters for use herein include cetyl palmitate and glycerylmonostearate. Cetyl alcohol and stearyl alcohol are preferred alcohols. A particularly preferred lipid vehicle material is comprised of a mixture of cetyl alcohol

and stearyl alcohol containing from about 55% to about 65% (by weight of mixture) of cetyl alcohol.

If included in the compositions of the present invention, the lipid vehicle material is typically present at from about 0.1% to about 10.0% of the composition; the cationic surfactant vehicle material is present at from about 0.05% to about 5.0% of the composition.

The use of nonionic cellulose ethers and water-soluble gums for thickening compositions are also contemplated. See for example, U.S. Patent 4,557,928, Glover, issued December 10, 1985, teaching a hair conditioner comprising a suspension system which consists of one of glucan gum, guar gum, and hydroxyethylcellulose; and U.S. Patent 4,581,230, Grollier et al., issued April 8, 1986, which teaches cosmetic compositions for treating hair which comprise as thickening agents hydroxyethylcellulose, or water-soluble vegetable thickening agents, such as guar gum, each incorporated herein by reference.

Cellulose ethers useful for producing viscous compositions include those having a sufficient degree of nonionic substituents selected from the group consisting of methyl, hydroxyethyl, and hydroxypropyl to cause them to be water-soluble and which are further substituted with a hydrocarbon radical having from about 10 to 24 carbon atoms in an amount between about 0.2 weight percent and the amount which renders said cellulose ether less than 1%, by weight, soluble in water. The cellulose ether to be modified is preferably one of low to medium molecular weight; i.e., less than about 800,000 and preferably between about 20,000 and 700,000 (about 75 to 2500 D.P.).

Nonionic water-soluble cellulose ethers are preferred polymers that can be employed in hair care compositions. Widely used, commercially-available nonionic cellulose ethers include methyl cellulose, hydroxy propyl methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose and ethyl hydroxyethyl cellulose.

Other thickening agents for use in the compositions of the present invention, especially for hair rinses, include combinations of hydrophobically-modified polymeric materials with surfactants, such as quaternary ammonium compounds (such as ditallowdimethyl ammonium chloride). These vehicles are described in detail in the following patents: U.S. Patent 5,106,609, issued April 21, 1992 to Bolich et al., U.S. Patent 5,100,658, issued March 31, 1992 to Bolich et al., U.S. Patent 5,104,646, issued April 14, 1992 to Bolich et al, and U.S. Patent 5,100,657, issued March 31, 1992 to Ansher-Jackson et al., each incorporated herein by reference. By "hydrophobically modified nonionic water-soluble polymer" is meant a nonionic water-soluble polymer which has been modified by the substitution with a

sufficient amount of hydrophobic groups to make the polymer less soluble in water. By "water-soluble" what is meant is the polymer or salt, thereof, constituting the polymer backbone of the thickener should be sufficiently soluble such that it forms a substantially clear solution when dissolved in water at a level of 1%, by weight of the solution, at 25°C. Hence, the polymer backbone of the primary thickener can be essentially any water-soluble polymer. The hydrophobic groups can be C₈ to C₂₂ alkyl, aryl alkyl, alkyl aryl groups and mixtures thereof. The degree of hydrophobic substitution on the polymer backbone should be from about 0.10% to about 1.0%, depending on the particular polymer backbone. More generally, the ratio of hydrophilic portion to hydrophobic portion of the polymer is from about 10:1 to about 1000:1.

Nonionic water-soluble cellulose ethers are preferred to be employed as the polymer substrate of these hydrophobically modified polymers. Thus, e.g., hydroxyethyl cellulose, hydroxypropyl cellulose, methyl cellulose, hydroxypropyl methyl cellulose, ethyl hydroxyethyl cellulose, and methyl hydroxyethyl cellulose can be used.

It is also contemplated to utilize a suspending agent to thicken the compositions and/or suspend the insoluble ingredients of the composition. Suitable suspending agents are long chain acyl derivatives, long chain amine oxides, and mixtures thereof, wherein such suspending agents are present in the shampoo compositions in crystalline form. A variety of such suspending agents are described in U.S. Patent Reissue 34,584, Grote et al., issued April 12, 1994. Especially preferred is ethylene glycol distearate.

Also included among the long chain acyl derivatives useful as suspending agents are the N,N-di(hydrogenated) C₈-C₂₂ (preferably C₁₂-C₂₂, more preferably C₁₆-C₁₈) amido benzoic acid, or soluble salt (e.g., K, Na salts) thereof particularly N,N-di(hydrogenated)tallow amido benzoic acid which is commercially marketed by Stepan Company (Northfield, Illinois, USA).

Another component useful in the compositions for thickening or for suspending insoluble ingredients herein is a crosslinked carboxylic polymeric thickener. These crosslinked polymers contain one or more monomers derived from acrylic acid, substituted acrylic acids, and salts and esters of these acrylic acids and the substituted acrylic acids, wherein the crosslinking agent contains two or more carbon-carbon double bonds and is derived from a polyhydric alcohol.

Examples of commercially available carboxylic acid polymers include the carbomers, which are homopolymers of acrylic acid crosslinked with allyl ethers of sucrose or pentaerytritol. The carbomers are available as the Carbopol® 900 series

from B.F. Goodrich. Examples of commercially available copolymers also include copolymers of C₁₀₋₃₀ alkyl acrylates with one or more monomers of acrylic acid, methacrylic acid, or one of their short chain (i.e. C₁₋₄ alcohol) esters, wherein the crosslinking agent is an allyl ether of sucrose or pentaerythritol. These copolymers are known as acrylates/C₁₀₋₃₀ alkyl acrylate crosspolymers and are commercially available as Carbolpol® 1342, Pemulen TR-1, and Pemulen TR-2, from B.F. Goodrich.

When used, the compositions of the present invention will generally comprise from about 0.01% to about 2%, more preferably from about 0.05% to about 1% and most preferably from about 0.10% to about 0.75% of the carboxylic acid polymer thickeners.

Other thickeners include: low pH thickening agents such as polyacrylamide, available as Sepigel from Seppic Corporation; and crosslinked methyl quaternized dimethylaminomethacrylate, available as Salcare SC95 from Allied Colloids.

15 Emulsifiers

The compositions herein can contain various emulsifiers. These emulsifiers are useful for emulsifying the various carrier components of the compositions herein, and are not required for solubilizing or dispersing the copolymers of the present invention. Suitable emulsifiers can include any of a wide variety of nonionic, cationic, anionic, and zwitterionic surfactants as disclosed above and as disclosed in the general literature. See, for example, McCutcheon's, Detergents and Emulsifiers, North American Edition (1986), published by Allured Publishing Corporation; U.S. Patent No. 5,011,681 to Ciotti et al., issued April 30, 1991; U.S. Patent No. 4,421,769 to Dixon et al., issued December 20, 1983; and U.S. Patent No. 3,755,560 to Dickert et al., issued August 28, 1973.

Suitable emulsifiers also include esters of glycerin, esters of propylene glycol, fatty acid esters of polyethylene glycol, fatty acid esters of polypropylene glycol, esters of sorbitol, esters of sorbitan anhydrides, carboxylic acid copolymers, esters and ethers of glucose, ethoxylated ethers, ethoxylated alcohols, alkyl phosphates, polyoxyethylene fatty ether phosphates, fatty acid amides, acyl lactylates, soaps and mixtures thereof.

Suitable emulsifiers also include, but are not limited to, polyethylene glycol 20 sorbitan monolaurate (Polysorbate 20), polyethylene glycol 5 soya sterol, Steareth-20, Cetareth-20, PPG-2 methyl glucose ether distearate, Ceteth-10, Polysorbate 80, cetyl phosphate, potassium cetyl phosphate, diethanolamine cetyl phosphate, Polysorbate 60, glyceryl stearate, PEG-100 stearate, and mixtures thereof. The emulsifiers can be used individually or as a mixture of two or more and can comprise

from about 0.1% to about 10%, more preferably from about 1% to about 7%, and most preferably from about 1% to about 5% of the compositions of the present invention.

Additional Components

5 The compositions herein can contain a variety of other optional components suitable for rendering such compositions more cosmetically or aesthetically acceptable, to improve storage stability and efficacy, or to provide them with additional usage benefits. Such conventional optional ingredients are well-known to those skilled in the art, e.g., colors and dyes, perfumes, pearlescent aids, such as
10 ethylene glycol distearate; preservatives, such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; thickeners and viscosity modifiers, such as a diethanolamide of a long chain fatty acid (e.g., PEG 3 lauric diethanolamide), cocomonoethanol amide, guar gum, methyl cellulose, starches and starch derivatives; fatty alcohols, such as cetearyl alcohol; sodium chloride; sodium sulfate; polyvinyl
15 alcohol; ethyl alcohol; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; salts, in general, such as potassium acetate and sodium chloride; coloring agents, such as any of the FD&C or D&C dyes; perfumes; sequestering agents, such as disodium ethylenediamine tetra-acetate; polymer plasticizing agents, such as glycerin, disobutyl
20 adipate, butyl stearate, and propylene glycol; vitamins and derivatives thereof (e.g., ascorbic acid, vitamin E, tocopheryl acetate, retinoic acid, retinol, retinoids, and the like; skin sensates, astringents, skin soothing agents, skin healing agents and the like, nonlimiting examples of these aesthetic components include panthenol and derivatives (e.g. ethyl panthenol), pantothenic acid and its derivatives, clove oil, menthol, camphor, eucalyptus oil, eugenol, menthyl lactate, witch hazel distillate,
25 allantoin, bisabolol, dipotassium glycyrrhizinate and the like.); polymers for aiding the film-forming properties and substantivity of the composition (such as a copolymer of eicosene and vinyl pyrrolidone, an example of which is available from GAF Chemical Corporation as Ganex^R V-220); preservatives for maintaining the antimicrobial
30 integrity of the compositions; skin penetration aids such as DMSO, 1-dodecylazacycloheptan-2-one (available as Azone from the Upjohn Co.); and the like. Such optional ingredients generally are used individually at levels of from about 0.01% to about 10.0%, preferably from about 0.05% to about 5.0%, of the composition.

35 Method of Using Topical Personal Care Compositions

The compositions of the present invention are used in conventional ways to provide the desired benefit appropriate to the product such as hair styling, holding,

cleansing, conditioning and the like for hair care compositions and benefits such as moisturization, sun protection, anti-acne, anti-wrinkling, artificial tanning, analgesic, and other cosmetic and pharmaceutical benefits for skin care compositions. Such methods of use depend upon the type of composition employed but generally involve application of an effective amount of the product to the hair or skin, which may then be rinsed from the hair or skin (as in the case of shampoos and some conditioning products) or allowed to remain on the hair (as in the case of spray, mousse, or gel products), or allowed to remain on the skin (as in the case of the skin care compositions). By "effective amount" is meant an amount sufficient to provide the benefit desired. Preferably, hair rinse, mousse, and gel products are applied to wet or damp hair prior to drying and styling of the hair. After such compositions are applied to the hair, the hair is dried and styled in the usual ways of the user. Hair sprays are typically applied to dry hair after it has already been dried and styled. Cosmetic and pharmaceutical topical skin care compositions are applied to and rubbed into the skin.

The following examples further illustrate preferred embodiments within the scope of the present invention. The examples are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

EXPERIMENTAL

Silicone macromers I and II and Polymers I, II, and III, can be synthesized according following procedures. There are numerous variations on these procedures which are entirely up to the discretion of the synthetic chemist (e.g., choice of degassing method and gas, choice of initiator type, extent of conversion, reaction loading, etc). The choice of initiator and solvent are often determined by the requirements of the particular monomers used, since different monomers have different solubilities and different reactivities to a specific initiator.

Synthesis of 1-(Dimethylchlorosilyl)-2-(p-styryl)ethane End-Cap

In a three neck round bottom flask equipped with a magnetic stirrer, a thermometer and an addition funnel, a solution of divinyl benzene (50.0g, 0.384 moles) and chlorodimethyl silane (11.113 g, 0.128 moles) is prepared in dry tetrahydrofuran (THF) (200 mL). To this solution, a chloroplatinic acid solution (0.150 g in 20 mL THF) is added dropwise. The reaction is highly exothermic, hence a slow addition of chloroplatinic acid is necessary. After the addition of platinic acid, the reaction is allowed to continue for an additional one hour, with stirring. This solution (10.64 M) is used to prepare styrene end-capped silicone macromer I, as described below.

Silicone Macromers I and II: In a round bottom flask which is equipped with a magnetic stirrer, a solution of hexamethylcyclotrisiloxane monomer (150 g) is prepared in dry cyclohexane (150 g). sec-Butyl lithium (0.0125 moles) initiator is added dropwise. The reaction mixture is allowed to stir for 10 minutes. This step is followed by the addition of THF (150 g) to the reaction mixture. The solution is stirred overnight, followed by heating at 50 deg C for 5 hours. The end-cap (0.025 moles) is then added slowly to the solution. Silicone Macromer I is made with the 1-(Dimethylchlorosilyl)-2-(p-styryl)ethane end-cap, as prepared above. The end-cap solution of the above end-cap synthesis is added dropwise. Silicone Macromer II is made with a chlorodimethylstyrylsilane end-cap, which can be prepared as described and shown in Holohan, George, Barrie, and Parker, "Monofunctional Polydimethylsiloxane Oligomers For Graft Copolymerization", Macromol. Chem. Phys. 195, 2965-2979 (1994). The end-cap from this synthesis is added dropwise to the solution. Alternately, the end-cap can be solubilized in THF and then added dropwise. The macromer is recovered by precipitating the final solution in methanol.

Polymer I: Place 20 parts acrylic acid, 63 parts t-butylacrylate, and 17 parts styrene end-capped polydimethylsiloxane macromer(Silicone Macromer I) in a flask. Add sufficient ethyl acetate or acetone (preferably acetone) as the reaction solvent to produce a final monomer concentration of 25%. Add initiator, azobisisobutyronitrile, to a level of 0.5% by weight relative to the amount of monomer. Purge the flask of oxygen by inserting an argon gas line below the surface of the liquid and allowing argon to bubble into the reaction solvent for about 15 minutes. Heat to 60°C and maintain this temperature for 48 hours while agitating. Terminate the reaction by cooling to room temperature, and dry off the reaction solvent by pouring the reaction mixture into a teflon-coated pan and placing in a vacuum oven.

Polymer II: Place 20 parts acrylic acid, 63 parts t-butylacrylate, and 17 parts styrene end-capped polydimethylsiloxane macromer(Silicone Macromer II) in a flask. Add sufficient ethyl acetate or acetone (preferably acetone) as the reaction solvent to produce a final monomer concentration of 25%. Add initiator, azobisisobutyronitrile, to a level of 0.5% by weight relative to the amount of monomer. Purge the flask of oxygen by inserting an argon gas line below the surface of the liquid and allowing argon to bubble into the reaction solvent for about 15 minutes. Heat to 60°C and maintain this temperature for 48 hours while agitating. Terminate the reaction by cooling to room temperature, and dry off the

reaction solvent by pouring the reaction mixture into a teflon-coated pan and placing in a vacuum oven.

- 5 Polymer III: Place 20 parts acrylic acid, 30 parts N-isopropylacrylamide, 35 parts t-butylacrylate, and 15 parts styrene end-capped polydimethylsiloxane macromer (Silicone Macromer I) in a flask. Add sufficient ethyl acetate or acetone (preferably acetone) as the reaction solvent to produce a final monomer concentration of 25%. Add initiator, azobisisobutyronitrile, to a level of 0.5% by weight relative to the amount of monomer. Purge the flask of oxygen by inserting an argon gas line below the surface of the liquid and allowing argon to bubble into the reaction solvent for about 15 minutes. Heat to 60°C and maintain this temperature for 48 hours while agitating. Terminate the reaction by cooling to room temperature, and dry off the reaction solvent by pouring the reaction mixture into a teflon-coated pan and placing in a vacuum oven.

EXAMPLES

- 15 The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention. Ethanol in the following formulas is anhydrous, unless
20 otherwise indicated.

EXAMPLES 1-4

Disclosed below are exemplary mousse compositions of the present invention.

	<u>Component (wt.%)</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
5	Polymer III	3.00	3.00	3.00	3.00
	Lauramine-oxide	0.10	0.10	0.00	0.10
	Cocamidopropyl betaine	1.33	1.33	0.30	1.33
	Propylene glycol	0.20	0.10	0.10	0.10
	Perfume	0.10	0.10	0.05	0.10
10	Disodium EDTA - dihydrate	0.10	0.10	0.10	0.10
	Phenoxyethanol	0.25	0.25	0.25	0.25
	Methyl paraben	0.15	0.15	0.15	0.15
	Polyquaternium-4 ¹	0.00	0.00	0.00	0.20
	Stearyltrimethylammonium				
15	chloride	0.00	0.00	0.20	0.00
	KOH Solution (45% active)	0.80	0.80	1.00	0.90
	Deionized Water	q.s.	q.s.	q.s.	q.s.

¹ Celquat L200, National Starch and Chemical Corp. (Bridgewater, NJ, USA,
20 copolymer of hydroxyethylcellulose and diallyldimethyl ammonium chloride.

The composition is made by mixing the silicone grafted copolymer in the water, with
the KOH solution, then sequentially adding the remaining ingredients, except for
perfume, with stirring, heating to 40°C - 60°C with stirring, and stirring for an
25 additional period of about eight hours while allowing the composition to cool at
ambient temperature, and then mixing in the perfume. The product can then be
packaged in a conventional aerosol or non aerosol mousse spray package.

EXAMPLES 5-8

Below are several exemplary reduced VOC hair spray compositions of the
30 present invention.

	<u>Component (wt.%)</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
	Polymer I or II	4.50	3.50	4.00	3.00
	Deionized Water	5.00	3.00	18.00	17.00
	Isododecane	1.50	0.00	0.00	0.00
35	KOH Solution (45% active)	0.90	0.65	0.00	0.75
	NaOH Solution (30% active)	0.00	0.00	1.00	0.00
	Triethyl Citrate	0.20	0.40	0.00	0.10

	Perfume	0.10	0.25	0.05	0.10
	Propylene Glycol	0.05	0.00	0.00	0.10
	N-Butane (Propellant)	7.50	6.00	0.00	0.00
	HFC 152A (Propellant)	15.00	17.00	0.00	0.00
5	Dibutyl Adipate	0.00	0.00	0.30	0.00
	SDA 40 Ethanol	qs	qs	qs	qs

The compositions are made by adding the ethanol to a mixing container first, followed by addition of the rest of the non-propellant ingredients sequentially in the order shown above, followed by vigorous stirring for two to three hours. The compositions of Examples 5 and 6 are then added to conventional aerosol cans in the conventional manner and charged with the propellants. The compositions of Examples are added to conventional nonaerosol pump spray containers.

EXAMPLE 9

The following is a shampoo composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
20	Ammonium laureth sulfate	5.00
	Cocamido propyl betaine	6.00
	Polymer III	4.00
	NaOH Solution (30% active)	0.10
	PEG 150 distearate	2.00
25	Glydant ¹	0.38
	Aminomethylpropanol	0.40
	Perfume	1.00
	Deionized Water	q.s.

¹Preservative commercially available from Glyco, Inc.

The shampoo is prepared by combining the ammonium laureth sulfate and Silicone Grafted Copolymer (Polymer III) and heating to 70°C for about 1/2 hour with mixing. The remaining ingredients are added and mixed for an additional 1/2 hour. The batch is then cooled to ambient temperature. The pH is adjusted to 6.5 by the addition of citric acid or sodium hydroxide, if necessary.

EXAMPLE 10

The following is a styling and conditioning hair rinse composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
5	Polymer III	3.00
	NaOH Solution (30% active)	0.90
	<u>Silicone Premix</u>	
	Silicone Gum GE SE76 ¹	0.50
	Decamethyl cyclopentasiloxane	4.00
10	<u>Main Mix</u>	
	Cetyl hydroxyethylcellulose ²	0.60
	Locust bean gum	0.50
	EDTA, disodium salt	0.15
	DTDMAC	0.65
15	Glydant ³	0.40
	Deionized Water	q.s.

¹Commercially available from General Electric

²Polysurf from Aqualon Co.

³Preservative commercially available from Glyco, Inc.

- 20 The Silicone Premix is blended separately by conventional means. The Main Mix is prepared by adding all the ingredients and heating to 95°C for 1/2 hour with agitation. As the batch is cooled to about 60°C, the Silicone Premix, Silicone Grafted Copolymer (Polymer III), and NaOH solution are added to the Main Mix with agitation and the batch is cooled to ambient temperature.

25

EXAMPLE 11

Reduced VOC hairspray compositions are prepared from the following components.

<u>Ingredients</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
Water	QS 100	QS 100	QS 100	QS 100
Ethanol	54.0	54.0	54.0	54.0
Polymer I, II, or III	4.0	3.0	4.0	3.0
KOH Solution (45% active)	0.80	0.60	1.00	0.75
Diocetyl Phthalate	0.40	---	0.10	---
Fragrance	0.05	0.2	---	---

These products are prepared by first dissolving the polymer in the ethanol with stirring. The remaining ingredients are then added with stirring. The resulting hair spray compositions can then be packaged in a nonaerosol spray pump. Alternatively, the compositions can be combined with conventional propellants and packaged in an aerosol spray container.

EXAMPLE 12

Mousse compositions are prepared from the following components utilizing conventional mixing techniques.

10

<u>Ingredients</u>	<u>Weight %</u>		
	<u>A</u>	<u>B</u>	<u>C</u>
Water	QS 100	QS 100	QS 100
Polymer III	3.00	2.50	3.50
NaOH Solution (30% active)	0.80	0.50	0.90
Lauramide DEA	0.33	0.33	0.33
Sodium Methyl Oleyl Taurate	1.67	1.67	1.67
DMDM Hydantoin	0.78	0.78	0.78
Disodium EDTA	0.20	0.20	0.20
Polyoxyalkylated isostearyl alcohol ¹	0.10	0.10	0.10
Fragrance	0.10	0.10	0.10
Propellant ²	7.0	7.0	7.0

These products are prepared by first dissolving the polymer in water with stirring. The remaining ingredients, except the propellant, are then added with stirring. The resulting mousse concentrate can then be combined with conventional propellants (e.g., Propellant A46²) and packaged in an aerosol spray. These mousses are useful for application to the hair to provide a styling and holding benefit.

15

¹ Aerosurf 66-E10.

² Available as a mixture of 82.46% isobutane, 16.57% propane, and 0.001% butane.

EXAMPLE 13

Hair tonic compositions are prepared from the following components utilizing conventional mixing techniques.

<u>Ingredients</u>	<u>Weight %</u>		
	<u>A</u>	<u>B</u>	<u>C</u>
Ethanol (190 Proof)	QS 100	QS 100	QS 100
Polymer I, II, or III	0.75	1.00	1.25
Aminomethyl Propanol	0.15	0.18	0.22
Fragrance	0.10	0.20	0.30

- 5 These products are prepared by dissolving the polymer in the ethanol with stirring and then adding the fragrance and any colors. These hair tonics are useful for application to the hair to provide a styling and holding benefit.

EXAMPLE 14

- 10 A conditioning and styling shampoo composition is prepared from the following components utilizing conventional mixing techniques.

	<u>Ingredients</u>	<u>Weight %</u>
	<u>Styling Agent</u>	
	Polymer III	3.00
15	NaOH Solution (30% active)	0.20
	<u>Premix</u>	
	Silicone gum	0.50
	Dimethicone, 350 cs fluid	0.50
	<u>Main Mix</u>	
20	Water	QS100
	Ammonium lauryl sulfate	11.00
	Cocamide MEA	2.00
	Ethylene glycol distearate	1.00
	Xanthan Gum	1.20
25	Methylchlorisothiazolinone (and)	
	methylisothiazolinone	0.04
	Citric Acid to pH 4.5 as needed	

- 30 The Main Mix is prepared by first dissolving the xanthan gum in the water with conventional mixing. The remaining Main Mix ingredients are added and the Main

- Mix is heated to 150^oF with agitation for 1/2 hour. The Styling Agent and the Premix are then added sequentially with about 10 minutes of agitation between additions, and the entire mixture is stirred while the batch is cooled to room temperature. For varied particile size, the Styling Agent and Premix can be added at different times using either or both high shear mixing or normal agitation.

EXAMPLE 15

Anti-Acne Composition

An anti-acne composition is made by combining the following components using conventional mixing technology.

10	<u>Ingredient</u>	<u>Weight %</u>
	Water	QS100
	Salicylic Acid	2.00
	Polymer I, II, or III	2.00
	Ethanol (SDA 40)	40.00
15	Aminomethyl Propanol	0.40

EXAMPLE 16

A topical analgesic composition is made by combining the following ingredients utilizing conventional mixing techniques.

20	<u>Ingredient</u>	<u>Weight %</u>
	Water, Purified	QS100
	Ibuprofen	2.00
	Polymer III	2.00
	Aminomethyl Propanol	0.45
25	Ethanol (SDA 40)	20.00

EXAMPLE 17

A composition for sunless tanning is made by combining the following ingredients utilizing conventional mixing techniques.

	<u>Ingredients</u>	<u>Weight %</u>
30	<u>Phase A</u>	
	Water	qs 100
	Polymer III	2.00
	NaOH Solution (30% active)	0.70

	Carbomer 934 ¹	0.20
	Carbomer 980 ²	0.15
	Acrylic Acid Copolymer ³	0.15
	<u>Phase B</u>	
5	PPG-20 Methyl Glucose Ether	
	Distearate	2.00
	Tocopheryl Acetate	1.20
	Mineral Oil	2.00
	Stearyl Alcohol	1.00
10	Shea Butter	1.00
	Cetyl Alcohol	1.00
	Cetareth-20	2.50
	Ceteth-2	1.00
	Ceteth-10	1.00
15	<u>Phase C</u>	
	DEA-Cetyl Phosphate	0.75
	<u>Phase D</u>	
	Dihydroxyacetone	3.00
20	<u>Phase E</u>	
	Butylene Glycol	2.00
	DMDM Hydantoin (and)	
	Iodopropynyl Butylcarbamate	0.25
	<u>Phase F</u>	
25	Fragrance	1.00
	Cyclomethicone	2.00

In a suitable vessel the Phase A ingredients are dispersed in the water and heated to 75-85 °C. In a separate vessel the Phase B ingredients are combined and heated to 85-90 °C until melted. Next, the DEA-Cetyl Phosphate is added to the liquid Phase B and stirred until dissolved. This mixture is then added to Phase A to form the emulsion. The emulsion is cooled to 40-45 °C with continued mixing. Next, in a separate vessel, the dihydroxyacetone is dissolved in water and the

resulting solution is mixed into the emulsion. In another vessel, the Phase E ingredients are heated with mixing to 40-45°C until a clear solution is formed and this solution is then added to the emulsion. Finally, the Phase F ingredients are added to the emulsion with mixing, which is then cooled to 30-35°C, and then to room temperature. This emulsion is useful for topical application to the skin to provide an artificial tan.

- 1 Available as Carbopol^R 934 from B.F. Goodrich.
- 2 Available as Carbopol^R 980 from B.F. Goodrich.
- 3 Available as Pemulen TR1 from B.F. Goodrich.

10

EXAMPLE 18Sunscreen Composition

An oil-in-water emulsion is prepared by combining the following components utilizing conventional mixing techniques.

	<u>Ingredients</u>	<u>Weight %</u>
15	<u>Phase A</u>	
	Water	QS100
	Carbomer 954 ¹	0.24
	Carbomer 1342 ²	0.16
	Polymer III	1.75
20	NaOH (30%)	0.70
	Disodium EDTA	0.05
	<u>Phase B</u>	
	Isoarachidyl Neopentanoate ³	2.00
	PVP Eicosene Copolymer ⁴	2.00
25	Octyl Methoxycinnamate	7.50
	Octocrylene	4.00
	Oxybenzone	1.00
	Titanium Dioxide	2.00
	Cetyl Palmitate	0.75
30	Stearoxytrimethylsilane	
	(and) Stearyl Alcohol ⁵	0.50
	Glyceryl Tribehenate ⁶	0.75

		Dimethicone	1.00
		Tocopheryl Acetate	0.10
		DEA-Cetyl Phosphate	0.20
		<u>Phase C</u>	
5		Water	2.00
		Triethanolamine 99%	0.60
		<u>Phase D</u>	
		Water	2.00
		Butylene Glycol	2.00
10		DMDM Hydantoin (and)	
		Iodopropynyl Butylcarbamate ⁷	0.25
		dL Panthenol	1.00
		<u>Phase E</u>	
		Cyclomethicone	1.00
15	1	Available as Carbopol ^R 954 from B.F. Goodrich.	
	2	Available as Carbopol ^R 1342 from B.F. Goodrich.	
	3	Available as Elefac I-205 from Bernel Chemical.	
	4	Available as Ganex V-220 from GAF Corporation.	
	5	Available as DC 580 Wax from Dow Corning.	
20	6	Available as Sychrowax HRC from Croda.	
	7	Available as Glydant Plus from Lonza.	

In a suitable vessel the Phase A ingredients are dispersed in the water and heated to 75-85°C. In a separate vessel the Phase B ingredients (except DEA-Cetyl Phosphate) are combined and heated to 85-90°C until melted. Next, the DEA-Cetyl Phosphate is added to the liquid Phase B and stirred until dissolved. This mixture is then added to Phase A to form the emulsion. The Phase C ingredients are combined until dissolved and then added to the emulsion. The emulsion is then cooled to 40-45°C with continued mixing. In another vessel, the Phase D ingredients are heated with mixing to 40-45°C until a clear solution is formed and this solution is then added to the emulsion. Finally, the emulsion is cooled to 35°C and the Phase E ingredient is added and mixed. This emulsion is useful for topical application to the skin to provide protection from the harmful effects of ultraviolet radiation.

EXAMPLE 19Facial Moisturizer

A leave-on facial emulsion composition is prepared by combining the following components utilizing conventional mixing techniques.

5	<u>Ingredient</u>	<u>Weight %</u>
	Water	QS100
	Polymer III	1.00
	NaOH Solution (30% active)	0.40
	Glycerin	3.00
10	Cetyl Palmitate	3.00
	Cetyl Alcohol	1.26
	Quaternium-22	1.00
	Glyceryl Monohydroxy Stearate	0.74
	Dimethicone	0.60
15	Stearic Acid	0.55
	Octyldodecyl Myristate	0.20
	Carbomer 1342	0.125
	Tetrasodium EDTA	0.10
	DMDM Hydantoin and Iodopropynyl	
20	Butyl Carbamate	0.10
	Carbomer 951	0.075

25

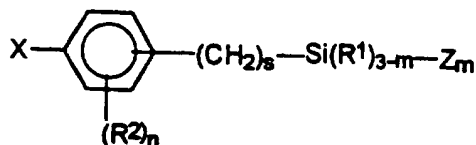
WHAT IS CLAIMED IS:

1. A topical personal care composition containing silicone grafted copolymer having improved resistance against hydrolysis, said composition being suitable for topical application to the skin or hair, and comprising:

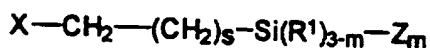
(a) from 0.1% to 50%, by weight of the composition, of silicone grafted copolymer containing:

(i) from 1% to 99%, by weight of the copolymer, of acid-containing monomers;

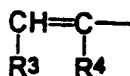
(ii) from 1% to 50%, by weight of the copolymer, of styrene end-capped or alkenyl end-capped silicone macromer having the formulas, respectively:



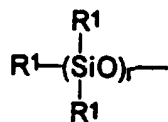
or



wherein: s is an integer from 0 to 6; m is an integer from 1 to 3, R² is C1-C10 alkyl or C7-C10 alkylaryl; n is an integer from 0 to 4; X is an ethylenically unsaturated group of the formula :



wherein R³ is -H or C1-C6 alkyl; R⁴ is H or C1-C6 alkyl; Z is



wherein each R¹ independently is an alkyl, aryl or alkylaryl having from 1 to 10 carbon atoms, and r is an integer from 4 to 700; and combinations thereof;

(iii) from 0% to 98% of additional monomers; and combinations thereof, and

(b) from 1% to 99.9%, by weight of the composition, of an aqueous or hydroalcoholic solvent for said silicone grafted copolymer suitable for application to the hair or skin, wherein said copolymer is soluble or dispersible in said solvent.

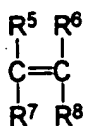
2. A composition as in Claim 1, wherein said silicone macromer is the styrene end-capped silicone macromer, n is 0, and said $-(CH_2)_s-Si(R^1)_3-m-Z_m$ of said silicone macromer is substituted at the para position relative to X wherein s is from 0 to 2, m is 1, n is 0, R^3 is H, R^4 is H or CH_3 , and R^1 is an alkyl, preferably wherein R^1 is methyl and r is from 50 to 500.

3. A composition according to any preceding Claim wherein said copolymer comprises from 1% to 50%, by weight of the copolymer, of said additional monomers, said additional monomers being nonionic, cationic, amphoteric, or a combination thereof, preferably wherein said additional monomers are nonionic monomers selected from the group consisting of acrylic and methacrylic acid esters of C1-C24 alcohols; styrene; alkylstyrenes; chloro-styrene; vinyl esters; vinyl chloride; vinyl toluene; vinyl caprolactam; vinylidene chloride; acrylonitrile; alpha-alkylstyrenes; 1,3-dialkenes; ethylenically monounsaturated hydrocarbons; alkoxyalkyl (meth)acrylates; alkyl vinyl ethers; di-acrylates and dimethacrylates; acrylamide; methacrylamide; diacetoneacrylamide; N,N-dialkyl(meth)acrylamides; N-alkyl(meth)acrylamides; acrylate and methacrylate alcohols; vinyl pyrrolidone; allyl alcohol; vinyl alcohol; and combinations thereof.

4. A composition according to any preceding Claim wherein said acid-containing monomers are selected from the group consisting of carboxylic acids and sulfonic acids.

5. A composition as in any preceding Claim wherein said acid-containing monomers are carboxylic acids.

6. A composition as in any preceding Claim wherein said carboxylic acid monomers are selected from the group consisting of those corresponding to the formula:



wherein: R^5 and R^6 independently are H or C1-C6 alkyl; R^7 is H, C1-C6 alkyl, or a carboxylic moiety having up to 12 carbon atoms; and R^8 is a carboxylic moiety having up to 12 carbon atoms; and mixtures thereof.

7. A composition as in any preceding Claim wherein said copolymer comprises:

- (i) from 5% to 90%, by weight of said copolymer, of said acid-containing monomers;
- (ii) from 2% to 40%, by weight of said copolymer, of said silicone macromers;
- (iii) from 0% to 70%, by weight of said copolymer, of said additional monomers.

8. A composition as in any preceding Claim wherein said copolymer comprises:

- (i) from 10% to 75%, by weight of said copolymer, of said acid-containing monomers;
- (ii) from 5% to 40%, by weight of said copolymer, of said silicone macromers;
- (iii) from 5% to 70%, by weight of said copolymer, of said additional monomers.

9. A composition as in any preceding Claim wherein said copolymer comprises:

- (i) from 15% to 50%, by weight of said copolymer, of said acid-containing monomers;
- (ii) from 5% to 25%, by weight of said copolymer, of said monomers derived from said silicone monomers;
- (iii) from 40% to 70%, by weight of said copolymer, of said additional monomers.

10. A hair spray product comprising the composition of any preceding Claim disposed within an aerosol or nonaerosol spray container.

INTERNATIONAL SEARCH REPORT

Intern. Publication No.

PCT/US 96/04183

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/06 A61K7/48

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 412 770 (MINNESOTA MINING & MFG) 13 February 1991 see claims 1-7 see page 4, line 55 - page 5, line 11 see page 5, line 55 - page 6, line 2 ---	1,3,4
X	WO,A,95 00108 (PROCTER & GAMBLE ;WELCH ROSEMARY JANE (GB); MARCHANT PHILIP JOHN () 5 January 1995 see claims 1-6 ---	1-7
A	WO,A,95 04518 (PROCTER & GAMBLE) 16 February 1995 see claim 1 see page 7, line 23 - page 10, line 25 ---	1,3-6
A	WO,A,93 23446 (PROCTER & GAMBLE) 25 November 1993 -----	

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- * "A" document defining the general state of the art which is not considered to be of particular relevance
- * "E" earlier document but published on or after the international filing date
- * "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- * "O" document referring to an oral disclosure, use, exhibition or other means
- * "P" document published prior to the international filing date but later than the priority date claimed

- * "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- * "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- * "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * "&" document member of the same patent family

Date of the actual completion of the international search

10 September 1996

Date of mailing of the international search report

20.09.96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (- 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (- 31-70) 340-3016

Authorized officer

McConnell, C

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat'l Application No.
PCT/US 96/04183

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0412770	13-02-91	US-A- 4981903	01-01-91
		AU-A- 5185293	27-01-94
		AU-A- 5918990	07-02-91
		CA-A- 2021570	08-02-91
		DE-D- 69022800	09-11-95
		DE-T- 69022800	15-05-96
		JP-A- 3081311	05-04-91
		JP-B- 7074256	09-08-95
		US-E- RE34958	30-05-95
		US-A- 5021477	04-06-91
WO-A-9500108	05-01-95	AU-A- 6910194	17-01-95
		BR-A- 9406849	16-04-96
		CA-A- 2165431	19-12-94
		EP-A- 0723433	31-07-96
WO-A-9504518	16-02-95	AU-A- 7336694	28-02-95
		CA-A- 2167483	16-02-95
		EP-A- 0712309	22-05-96
		FI-A- 960494	02-04-96
		NO-A- 960451	02-04-96
WO-A-9323446	25-11-93	AU-A- 4243393	13-12-93
		CA-A- 2135186	25-11-93
		CN-A- 1081195	26-01-94
		CZ-A- 9402773	16-08-95
		EP-A- 0640105	01-03-95
		FI-A- 945358	14-11-94
		HU-A- 70074	28-09-95
		JP-T- 7508060	07-09-95
		NO-A- 944303	13-01-95
		SK-A- 136194	09-08-95